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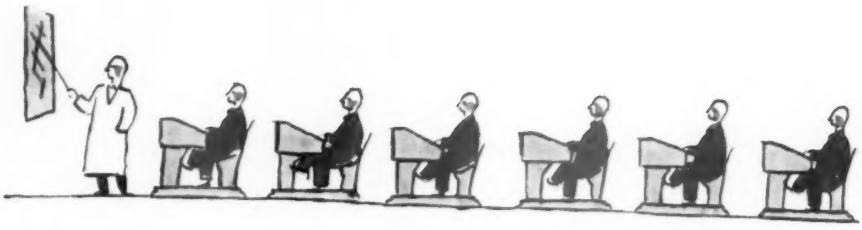
# Petroleum Technology

NOVEMBER, 1952



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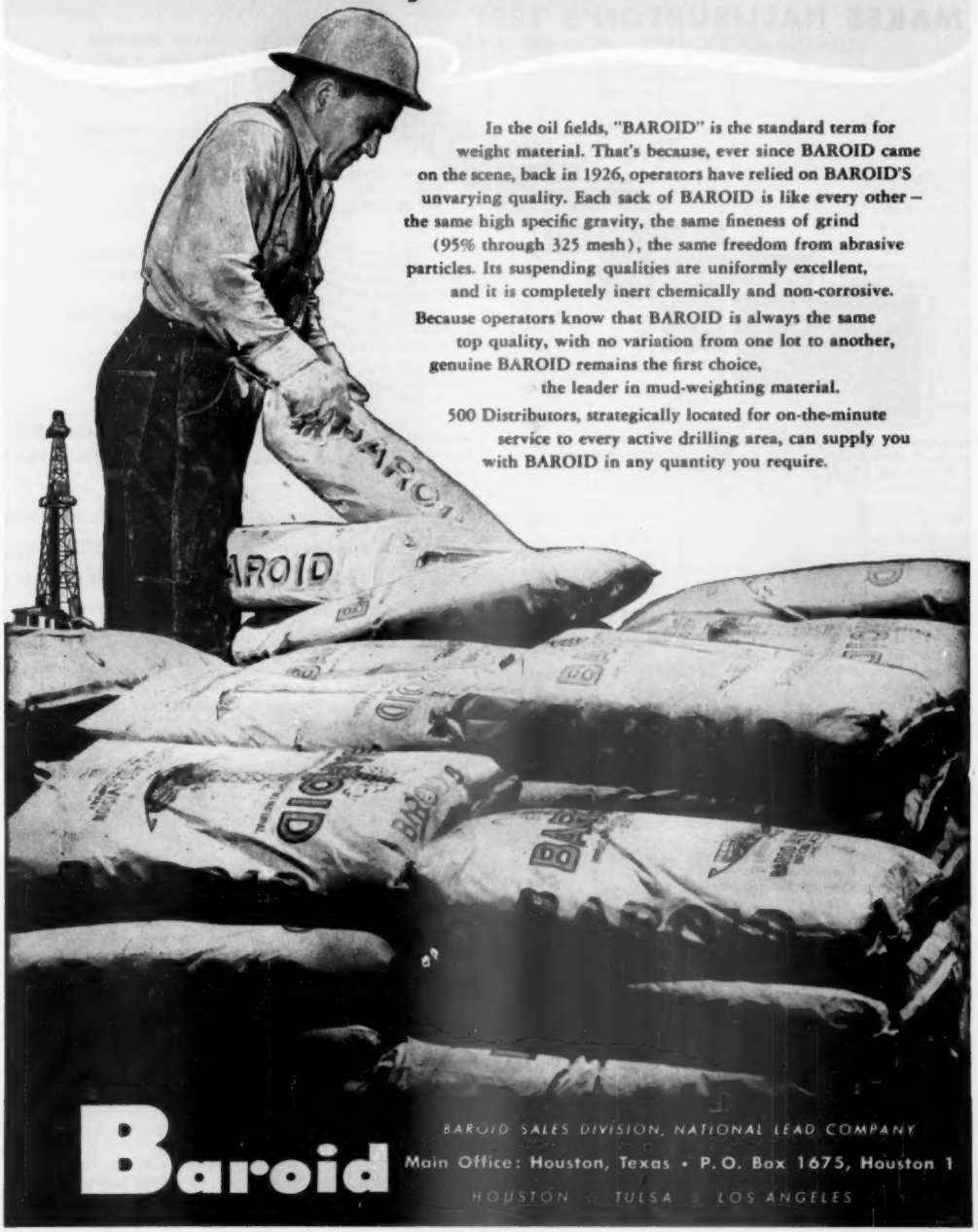


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# Journal of Petroleum Technology

Vol. IV NOVEMBER, 1952 No. 11

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*On the Cover* — Typical of the extremely mountainous topography of Colombia are these slopes of the Western Cordillera, down which the Buenaventura highway winds perilously. Development of the numerous sedimentary basins in this country is described in the article beginning on page 11. *Photo courtesy of Standard Oil Co. (N.J.)*

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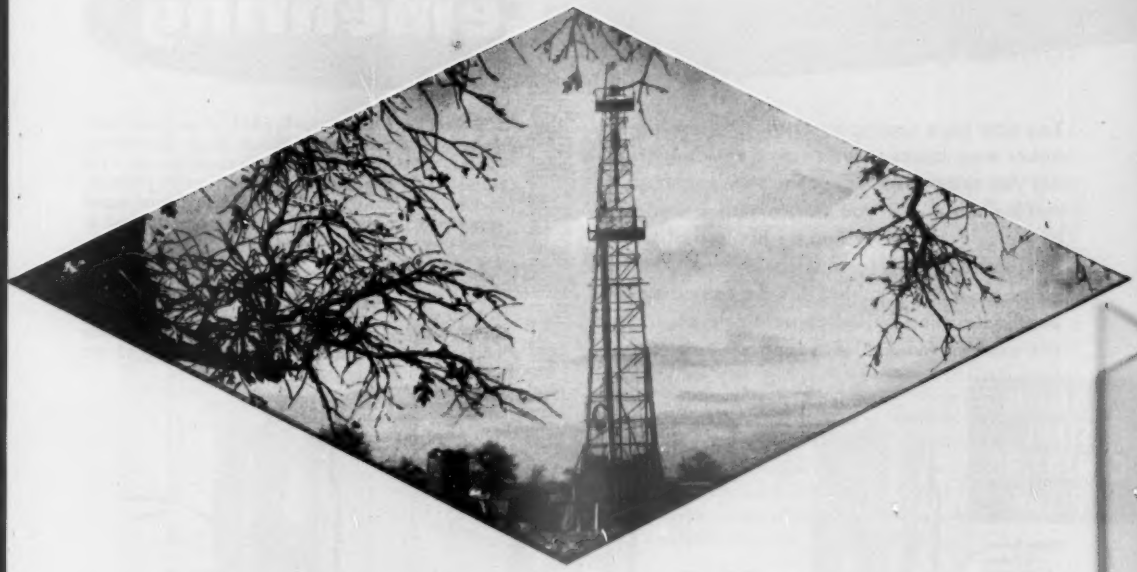

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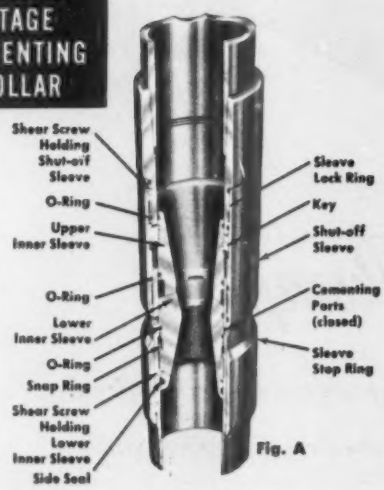


Fig. A

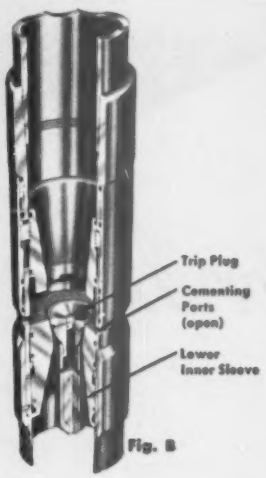


Fig. B

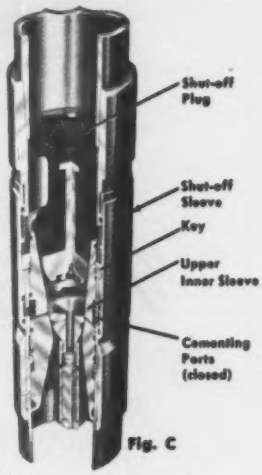


Fig. C

**Fig. A**—Ready for cementing the first stage. The cementing ports are covered by the Lower Inner Sleeve which is held in position by shear screws; shear screws also hold the Shut-Off Sleeve above the cementing ports. The Baker Flexible Cementing Plug (shown on opposite page) will pass through the Stage Collar without shearing the screws holding the Inner Sleeves.

**Fig. B**—Ready for cementing the second stage. After the Trip Plug is seated, application of hydraulic pressure shears the screws holding the Lower Inner Sleeve which moves downward, thus uncovering the cementing ports. The Trip Plug prevents passage of fluid into the casing below, and cement pumped into the casing will now pass through the cementing ports for the second-stage cementation.

**Fig. C**—Second-stage cementation is completed. The Shut-Off Plug has been pumped down the casing and pressure applied to shear the screws and move the Shut-Off Sleeve downward to close off the cementing ports. Note how the Sleeve Lock Ring has expanded to lock the Shut-Off Sleeve in position permanently covering the cementing ports.

***See opposite page for details of operation.***

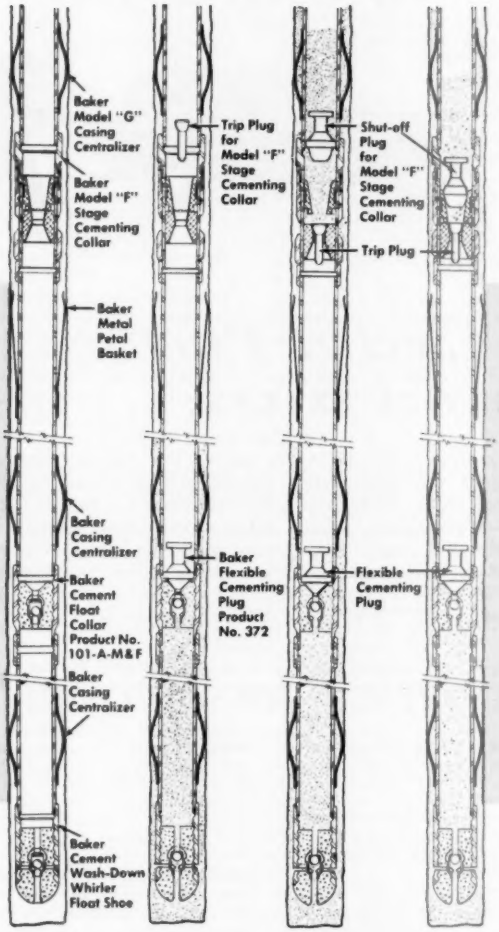
**2** The cementing ports of the Stage Cementing Collar may be opened at any time after completion of the first stage, and fluid may be circulated through the stage collar for any desired length of time before starting second-stage cementing.

**3** Operation of the stage collar is effected by fluid pressure applications only, and no movement of the casing is required after the first stage of the cementation has been completed.

**4** All internal parts of the Baker Stage Cementing Collar are constructed of readily drillable materials, and when drilled out there are no sharp shoulders or irregularities to interfere with the subsequent passage of tools through the collar.

**5** Since the steel Shut-off Sleeve is on the outside of the Stage Cementing Collar, there is no possibility of accidentally opening the cementing ports when drilling out the internal mechanism, or later when bits or casing scrapers are run through the collar.

# Here's how a typical **two-stage** cementing job is performed with the **Baker** Stage Cementing Collar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Trip Plug for Model "F" Stage Cementing Collar
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Shut-off Plug for Model "F" Stage Cementing Collar
Trip Plug
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Figure 1 Figure 2 Figure 3 Figure 4

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*Fig. 1—Hook-Up in Running-In and Mud-Conditioning Position.* The string (starting at bottom) consists of a Baker Cement Wash-Down Whirler Float Shoe for conditioning the hole, washing away bridges, and cementation of the lower (first) stage. Baker Casing Centralizers are positioned at strategic points (as illustrated) to center the casing, ensure annular clearance, and avoid channeling of the cement slurry. Next above is a Baker Cement Float Collar with Seat for Flexible Plug, Product No. 101-A M.& F. A Baker Metal Petal Basket (optional equipment) is positioned just below the Stage Cementing Collar to retain all cement slurry *above* the Basket when the second-stage cementation is performed. Note that Baker Casing Centralizers are used just above the Stage Cementing Collar to ensure annular clearance for the upward movement of the cement slurry.

*Fig. 2—The first-stage cement job has been completed.* The Flexible Plug has been pumped through the Stage Collar to its seat in the bevelled top of the Float Collar where it prevents over-pumping and also separates the cement slurry from the follow-up fluid. The Trip Plug has been placed in the casing and is gravitating to its seat in the Lower Inner Sleeve of the Stage Collar; see also Fig. B on opposite page. Application of hydraulic pressure, after the Trip Plug is seated, will result in opening of the cementing ports.

*Fig. 3—The second-stage cement job is almost completed.* The cement slurry has passed through the open ports, and the Shut-Off Plug (acting as a separator) is approaching its seat in the Upper Inner Sleeve of the Stage Collar. Note how the Baker Metal Petal Basket has prevented downward movement of the cement.

*Fig. 4—Both stages have now been successfully cemented.* The cementing ports are closed off by the Shut-Off Sleeve which is locked in position as shown in Fig. C on opposite page. When the cement has set, the readily drillable internal mechanism of the Baker Stage Cementing Collar, Float Collar and Float Shoe are removed by the drilling bit leaving the full I.D. of the casing free from any sharp shoulders or other obstructions, ready for all subsequent operations.

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# Petroleum Development of Colombia

By Victor Oppenheim
*Consulting Geologist and Engineer*
*Member AIME*

Colombia, in the northwestern part of South America, presents challenging problems in the development of her potential oil reserves. Although the country occupies a territory of 439,828 square miles and is roughly twice the size of Texas, its petroleum geology has been studied only in broad lines of surface observations with very limited and totally inadequate exploratory borings. Thus, since 1905 when modern search for oil began in Colombia, only about 200 wildcats have been drilled, most of these being shallow borings grouped together in isolated areas.

Considering the vast extent of the sedimentary basins in the country it becomes evident that, although the development progress has been continuous over many years, much more can be expected from Colombian oil production when the many prospective basins will become better known and more adequately tested.

## SEDIMENTARY BASINS

The complex tectonic history of Colombia is expressed in the extremely mountainous topography, which accounts for the development of numerous sedimentary basins. The principal basins are of Tertiary age and are, in most instances, underlain by marine, early Tertiary or Cretaceous sediments. Considering the vast areas covered by the basins, it is evident that the thickness of their sedimentary sections varies greatly between the peripheries and the zones of deep deposition. Also the geologic and stratigraphic conditions within each basin show marked differences in character and facies of sedimentation. In some instances of Tertiary beds, faunal correlations could be established with Tertiary deposits of Panama, Venezuela and Peru.

In a broad outline the Colombian sedimentary basins can be grouped and subdivided as follows:

The Northern Coastal Basin is composed of five secondary basins: lower Rio Magdalena valley, Rio Sinu valley, Rio San Jorge valley, Rio Cesar valley and the Goajira Peninsula. The Tertiary beds in all these areas differ somewhat in conditions of deposition, and although they are predominantly marine, continental facies are known to exist in parts of the lower Magdalena and San Jorge basins.

The Southern Maracaibo Basin on the Venezuelan border consists of a complete Tertiary section overlying well developed Cretaceous sediments.

The Pacific-Atrato Basin extends along about 800 kilometers between the boundary with Ecuador on the Pacific coast and the mouth of Rio Atrato on the Caribbean.

The Middle and Upper Magdalena Basin continues south of El Banco in a narrow inter-Andean belt to the headwaters of the Rio Magdalena. The Tertiary and Cretaceous sediments are here well developed; however, continental facies seem to set in in the southernmost part of the basin.

The Llanos Basin can be divided into the Northern Llanos Basin north of the Macarena massive and the Southern Llanos Basin south of the massive. Tertiary sediments of great thickness can be expected in the Northern Llanos which merge with southern Venezuela, of which they are a continuation. However, little is known as yet of the Tertiary stratigraphy of these two vast basins of the Llanos.

At the present state of geological knowledge of all these basins their ultimate petroleum possibilities are unpredictable, but, it can be estimated that the five principal basins probably cover in excess of 50,000,000 acres of lands suitable for petroleum exploration with possibilities varying from outstanding to favorable or mediocre.

## CONCESSIONS AND OIL FIELDS

Colombian yearly production for 1951 was 38,148,929 bbl. This production was derived from seven producing concessions covering 17 oil fields. The concessions are: One in the Northern

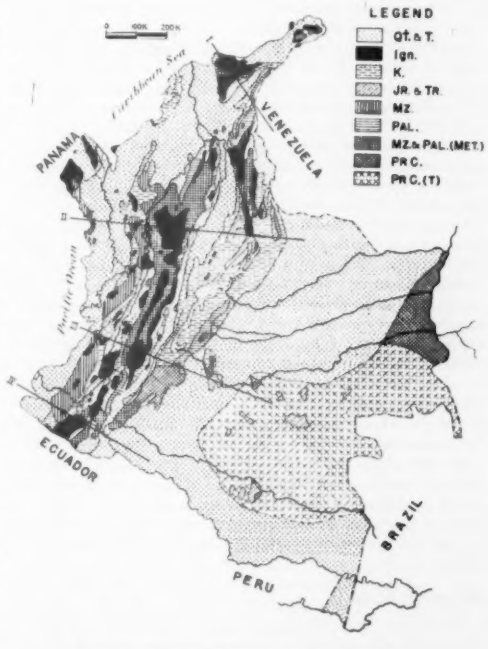


FIG. 1 — GEOLOGIC ELEMENTS OF COLOMBIA.

Coastal Basin (Dificil), one in the Southern Maracaibo Basin (Barco), five in the Middle and Upper Magdalena Basin (De Mares, Yondo, Cantagallo, Teran-Guaguaqui and Ortega). The recently discovered Totumal Field in the Magdalena Basin is not considered in the 1951 figures.

At present the more accessible and geologically suitable areas of the sedimentary basins are covered by about 500 concessions and private land leases, which include those in production, exploration or subject to future, final government contracts. The concessions granted by the government are of 50,000 hectares (123,500 acres) each, in all parts of the country except the Llanos of Eastern Colombia, where they can be of 100,000 hectares (247,000 acres) each. They are owned and controlled mainly by: the International Petroleum Co. of Colombia, the Richmond Petroleum Co., the Shell Oil Co., the Texas Oil Co., the Socony-Vacuum Oil Co., Empresa Colombiana de Petroleos (De Mares Concession) and the Allen Guiberson interests (Floresanto II Concession). The Floresanto II Concession is the only exploration concession owned by private interests at present in Colombia.

The bulk of Colombian production is accounted for by the four main oil concessions: De Mares, Barco, Yondo and Dificil. Their historical development, past and present production and geologic outline of their structures represent a complete review of the Colombian petroleum industry from its early beginnings to the present.

## THE DE MARES CONCESSION

The granting of the De Mares Concession marks the beginning of petroleum activity in Colombia. This concession, a large tract of land on the Magdalena River, was granted by the government in 1905 to the Frenchman, Robert De Mares. In 1916 De Mares transferred his concession to the Benedum-Trees interests of Pittsburgh and the first operating company (Tropical Oil Co.) was formed with rights to the 1,264,000 acres of the concession. However, the exploitation of the concession did not begin until 1922 when it was again transferred, to the Standard Oil Co. of New Jersey. Full-scale production was not initiated until 1926 when the pipeline to Mamonal near Cartagena was completed. The original contract with the government, which was for 30 years, lapsed in August of 1951. At present the concession is operated by the Empresa Colombiana de Petroleo under the technical supervision of the International Petroleum Co. which also operates the Barranca Bermeja refinery and owns the Andean National Corp.'s 669-mile pipeline. The four oil fields of the concession, Infantas, La Cira, Colorado and Galan, had in 1951 a total of 1,042 wells and had produced 13,591,089 bbl of oil. The cumulative production of the concession to the end of 1951 was 416,978,870 bbl. Thus, it is producing about 40 per cent of Colombia's oil, but the estimated reserve of the proved 18,711 acres is only about 125,000,000 bbl. It can be assumed that this does not cover the ultimate possibilities of the whole concession.

The De Mares Concession occupies the area between Rio Sogamoso and Rio Carare in the Middle Magdalena valley, some 300 miles from the mouth of the Magdalena River. Approximately seven conspicuous, surface structures were tested in this area. However, the main production of the De Mares Concession comes from two structures on which are located its two principal fields: Infantas Field and La Cira Field.

### Infantas Field

Production was discovered here in 1919. The structural features of this field appear as an anticline, faulted along its eastern flank. The anticline trends north 15° east with the fault plane dipping 45° east. The field is approximately seven miles long and about one mile wide. The structure is divided into a series of blocks by east-west trending faults.

Production comes from the Eocene, Chorro Series, known as "C" Zone and from Oligocene, Mugrosa Series or Upper "B" Zone. The underlying Cretaceous Lisama formation has thus far proved barren. The main production comes from the Eocene "C" Zone at a depth of 2,200-2,600 ft. The "B" Zone is reached at an average depth of 1,500 ft.

### La Cira Field

The La Cira Field is approximately five miles long by four miles wide and is located on an anticline, which was found to be productive in 1926. The anticline is asymmetrical and thrusted to the east, contrary to the Infantas anticline, which is thrusted to the west. It is also faulted along the east side, with faults trending north-south. East-west faulting is also present.

The three producing horizons are known as "A" Zone from the Colorado Series, "B" Zone from the Mugrosa Series, both of Oligocene age, and "C" Zone from the Chorro Series of Eocene age. The main production comes from the "C" Zone, similar to the Infantas Field. The "C" Zone is reached at a depth of 2,200-4,100 ft. The "B" Zone of the Mugrosa Series is found at a depth of about 1,100-1,600 ft. The "A" Zone in the Lower Oligocene, Colorado Series is found at about 600-1,000 ft. The thickness of the oil sands varies from 30 to 350 ft. The underlying Cretaceous has, thus far, proven barren also in the La Cira Field.

FIG. 2 — MAP SHOWING CONCESSIONS AND FIELDS, COLOMBIA.

## THE BARCO CONCESSION

The Barco Concession on the Venezuelan border was originally granted to Virgilio Barco in 1905 and extended over about 1,000,000 acres. In 1917 it was transferred to the Henry Doherty interests, which formed the Compania Colombiana de Petroleo. This company drilled the first producing well (1,500 bbl) at Rio de Oro in 1920. After a long period of subsequent inactivity the operating company, in turn, transferred the Barco Concession, in 1931, to the Gulf Oil Corp. The latter, not convinced of the possibilities of the concession, at the time, sold it to the Colombian Petroleum Co., owned jointly by the Socony-Vacuum and Texas Oil companies. The concession has since been reduced to 460,000 acres. However, the South American Gulf Oil Co. operates the 263-mile, 12-in. pipeline which connects the concession with the Caribbean port of Covenas. At the end of 1951 the seven oil fields developed on the concession had 123 producing wells, with a yearly production to the end of the same year, of 19,103,735 bbl. The cumulative production up to the end of 1951 was 73,474,117 bbl. The total proved area is estimated at 23,710 acres. The ultimate reserves are estimated to be very considerable.

The geology and all other features of th Barco Concession were amply described in a paper by Notestein, Human and Bowler.[5] The area is located in the Southern Maracaibo Basin on the Upper Rio Catatumbo. The geology is made up of Cretaceous and Tertiary sediments. The thickness of the Cretaceous varies from about 4,000-7,000 ft, while the Tertiary beds vary from 6,800-11,500 ft. The main production comes from the Lower Cretaceous and Lower Eocene beds. Five producing horizons are known in the Cogollo Limestone Series and three in the underlying Uribante Formation. The structural conditions controlling accumulations are due to normal and faulted anticlines.

About 12 main anticlinal or domal structures are outlined in the Barco Concession. The main production comes from about seven structures. These are: Petrolea (North Dome), Petrolea (South Dome), Rio de Oro, Carbonera, Tres Bocas, Socuavo and Tibu.

The Petrolea structure is one of the most important of the concession. It is a complexly faulted anticline, asymmetric with a steep west and gentle east flank. It consists of two parts known as the North and South Domes. The North Dome is the most productive and production comes from La Luna and Uribante Formations. The proved area of the Petroleum anticline is about 4,200 acres and, like other structures of the Barco Concession, shows many oil and gas seeps. The production is reached at depths from 99 to 1,953 ft.

The other fields are also located on anticlines or faulted anticlines and their production comes from Eocene, in the Catatumbo Formation on the Rio de Oro anticline, the Barco Formation from the Tres Bocas structure, and the Los Cuervos Formation from the Carbonera Field. The Tibu anticline is considered to be the northern continuation of the Sardinata structure. The Oligocene Carbonera Formation crops out on the crest of the fold. Basement rocks were reached on this structure at 9,227 ft. The Tibu member of the Uribante Formation, of lower Cretaceous age has proven to be an important producing zone of the structure. The average depth of the wells is of 4,000-5,000 ft.

## THE YONDO CONCESSION

The Yondo Concession has the third largest oil field in Colombia, the Casabe Field, which was discovered in 1941. The concession, of 120,000 acres, faces the De Mares Concession and is situated in the Departmento de Antioquia on the west side of the Magdalena River. It was originally held by the Tropical Oil Co. in virtue of a government contract of 1938. After several years of geological and geophysical surface work and several borings, the concession was released and abandoned as non-commercial in 1940. After being transferred by the government to the Shell Oil Co., the latter discovered the Casabe Field. The field had in 1951 a total of 259 producing wells with a total production to the end of the same year of 12,832,905 bbl. The output of the field has been growing constantly and at present it accounts for more than 30 per cent of Colombian crude. The cumulative production of the estimated 5,000 proved acres of the Casabe Field was 44,025,613 bbl to the end of 1951, and the reserves are still substantial.

The production of the Casabe Field is derived from unconsolidated sands in a faulted anticlinal structure. The producing beds are of Miocene, Oligocene and Eocene ages, known as "A," "B" and "C" sands. The depth to the top of the pay is 2,100 ft for the "A" and 3,720 ft for the "B" and "C" sands. The bottom of the pay is reached at 3,970 ft and 5,660 ft.

## THE DIFICIL CONCESSION

The Dificil Field of the Shell Oil Co. in the Departmento de Magdalena was discovered in 1943. It has 14 flowing wells with a daily production of about 3,000 bbl, and the cumulative production through 1951 was about 5,000,000 bbl. The field has considerable gas and a 20 MMcf/D natural gasoline plant is being completed by the Shell-Condor Co.

The proved area of the Dificl Field is 2,500 acres. The production comes from an Oligocene reef limestone found at 5,200 to 5,900 ft. The thickness of the pay is 28 ft. The gravity of the oil is over 40° API.

## OTHER CONCESSIONS

Of the others, the Totumal Concession, covering about 120,000 acres in the Middle Magdalena Basin in the Departamento de Magdalena, with its newly discovered Totumal Field, is an example of unexpected achievement. The concession was originally owned by the Richmond Petroleum Co. After being released by the latter in 1948, it was granted to the International Petroleum Co. The field was discovered by this company through its first (1,100 B/D) wildcat in November of 1951. The discovery well was completed three months after the company had returned the De Mares concession to the government. Although the ultimate potential of the field is, as yet, unknown, the Totumal well has revealed the presence of important hitherto unsupected Cretaceous production in the Middle Magdalena Basin, indicating the potentialities of reservoir beds in the widespread Cretaceous formations underlying the Tertiary basin covers. However, the source of Columbian oil is not of Cretaceous age alone, as was believed in the past. Eocene and Oligocene formations can be considered also to contain source rocks in some of the basins.

The Floresanto Concession in the Sinu Basin on the Caribbean coast, now in exploration, is another area of characteristically complex geological conditions. The shallow production of 51° API oil in the Miocene beds of the eastern flank of the thrusted Floresanto anticline undoubtedly indicates the presence of large oil accumulations in the underlying Oligocene, Charrura Formation. Deep-seated source beds represented in this basin by the, presumably Eocene, but possibly Cretaceous, La Risa limestones are found in the region in association with numerous active oil seeps. The Sinu Basin, composed of totally marine sediments, reaching in places over

20,000 ft in thickness, shows the most favorable indications of potential oil fields. However, to date it has been scarcely explored and remains untested as to its subsurface petroleum geology.

The above outline of the main Colombian producing oil fields and some of its concessions indicates that the real development of this country's oil reserves and potentialities is still in its initial stages. New fields many times the present production can be expected in the future.

There are at present about 2,500,000 acres of prospective oil lands covered by 24 exploration and exploitation concessions under contract with the government. This does not include the concessions in established exploitation. The recent growth of interest in Colombian petroleum prospects is best reflected by the considerable increase of applications for concessions, which in 1952 reached several million acres, as compared to less than 500,000 acres in 1949 and 1950.

## PIPELINES

Although Colombia's daily production for 1951 was 105,346 bbl, it is at present 106,242 bbl and its actual potential of the combined fields is 124,000 B/D. Yet the production is greatly limited by pipeline and refinery capacities.

Of the four crude oil pipelines in the country totaling 993 miles, only two serve as outlets to the Caribbean coast. The South American Gulf Oil Co.'s 12-in. pipeline from Petrolea to Covenas extends for 263 miles with 28,000 B/D capacity. The Andean National Corp.'s 10-in. and 12-in. pipeline from El Centro to Mamonal extends for 660 miles with 65,000 B/D capacity. The other two pipelines connect the Casabe and Dificil Fields of the Shell Oil Co. to the main Andean National Corp.'s pipeline. They have a capacity of 50,000 and 12,000 B/D respectively. The pipeline from Casabe to Galan is of 10-in. extending for only six miles. The line from Dificil to Plato is of 6-in. and 10-in. and runs for 55 miles.

With the serious limitations of the existing crude carrying pipelines, further expansion of production will have to be restricted and with it the wildcat activity in areas distant from the coast. Unless new substantial discoveries are made it is unlikely that the existing pipelines will be enlarged. The great cost of pipeline construction in Colombia, due to its very broken topography, naturally limits the search for oil and wildcatting to the more accessible parts of the country. The proved reserves in less accessible areas would have to be very substantial to justify the high cost involved. This is also the principal reason for the lack of adequate exploration in the Llanos of Colombia, east of the Andes.

As to product pipelines, only two are operating. The International Petroleum Co.'s 65-mile, 6-in. line from El Centro to Puerto Berio along the Magdalena River with a capacity of 7,500 B/D and the Departmento de Cundinamarca 22,000

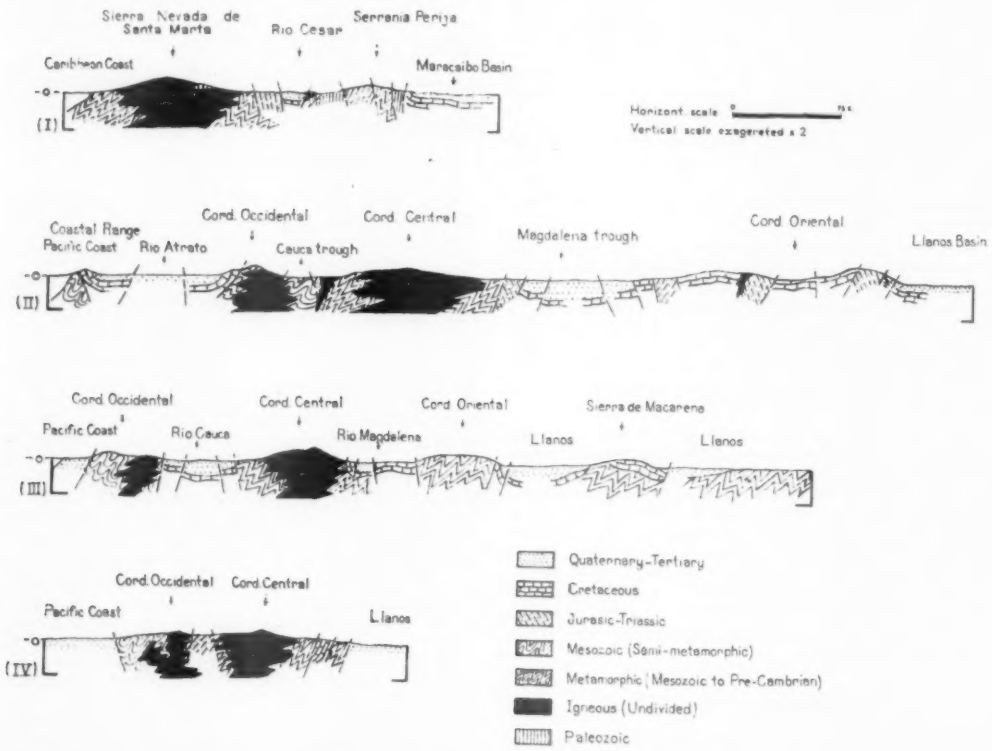


FIG. 3 — GENERALIZED GEOLOGIC SECTIONS, COLOMBIA.

B/D, 87-mile, 6⅝-in. line from Puerto Salgar to Bogota. Additional 280 miles of product lines are at present projected or under construction and will connect Beunaventura with Cali, Puerto Berio with Medellin and Puerto Berio with La Dorada.

The exportation of crude oil from Colombia has increased considerably in the last few years. Thus, it amounted to 28,268,872 bbl valued at 64.4 million dollars in 1950 as compared to 15,919,972 bbl valued at 36.4 million dollars for the first half of 1952.

## REFINERIES

There are only two refineries in operation in Colombia. The Barranca Bermeja 25,000 B/D topping and catalytic cracking plant serving the De Mares Concession is now owned by the Empresa Colombiana de Petroleos and at present is operated with the technical help of the International Petroleum Co. This refinery is being enlarged for a capacity of 35,000 B/D. The second refinery is a small 900 B/D skimming plant on the Barco Concession at Petrolea, and is owned and operated by the Colombian Petroleum Co.

A natural gasoline plant of 20 MMcf/D of gas is being built by the Shell-Condor Co. at Dificil. A 1,000 B/D pilot plant is also planned by the government.

The present refining capacity of Colombia is thus now limited to only 25,900 B/D, which is inadequate even for local consumption. Substantial amounts of refined products are imported, mainly for the consumption of the coastal and southern parts of the country. Local consumption has been increasing considerably. It is estimated that the 1952 consumption of refined products in the country will amount to 360 million gal, which represents a 14.6 per cent increase over the consumption of the previous year. Gasoline and lubricating oils are being imported mainly from Aruba and Curazao, while crude oils are exported through the coastal ports of Covenas and Mamonal terminals. The consumption of the Pacific Coast and southern parts of the country is supplied through imports from Talara, Peru, via the port of Buenaventura. Thus, the Barranca Bermeja refinery scarcely supplies the capital and the central, most populated parts of the country, while the rest of the country uses largely imported products. This unusual condition for a country of as great a potential as Colombia is largely due to, among other reasons, (1) topographic barriers and inadequate transportation systems, particularly between the northern and southern parts of the country; (2) lack of adequate wildcat exploration in the Coastal Basins, which, if developed, could make these regions independent of imported products.

## PETROLEUM RESERVES

Colombian yearly petroleum production to the end of 1951 was 38,148,929 bbl or equal to 0.91 per cent of the world total for the same year. Considering that to the end of 1941 it was less than 10,000,000 bbl, the production increased about four times in ten years through comparatively limited development and exploration activity. The 1951 production figure has been accounted for by a total of 1,450 producing wells including 157 flowing. The fact that 1951 production showed a substantial gain over 1950, and the discovery of three new fields in the same year indicate the evident possibilities in future production.

Colombian cumulative production to the end of 1951 was over 542,000,000 bbl. The estimated petroleum reserve given by Anderson[1] in 1941 as a maximum and based on the data available at the time was only 500,000,000 bbl.

Although exact figures of proved reserves are not available, it is evident that, in view of the estimated possibilities and recent discoveries, all previous estimates will have to be revised. The true potential production may be several times that of the estimated 1941 "maximum." Final data on proved reserves will, however, have to await future development. More intense wildcat exploration and sound petroleum policies will not fail to multiply the present production and the estimated potential reserve of Colombia.

## CONCLUSIONS

The above outline of the Colombian petroleum situation reflects the possibilities of the country. The main reasons for the fact that Colombian production is lagging far behind the potentialities of her sedimentary basins are:

1. Insufficient exploratory drilling, which in the past has been totally inadequate, considering the size and possibilities of the sedimentary basins.
2. Absence of independent oil operators who would contribute the necessary and healthy spirit of competitive exploration in the petroleum industry.
3. The cumbersome and slow-acting petroleum policies of the past.

The effects of more intense exploratory drilling is best illustrated by the discovery of three new oil fields due to three wildcats drilled in 1951. The last cause has been largely eliminated through the recent and ample, new governmental regulations.

These factors, when broadly applied to the Colombian petroleum industry should stimulate its growth and resurgence which should bring its production to a height and place corresponding with its real potentialities.

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***Magna-Tector Saves Fishing Jobs***

**3**

The Magna-Tector not only locates the stuck point in drill pipe, casing, or tubing, but many times indicates the sticking medium, and in some cases working and/or spotting oil in the tight place indicated by the Magna-Tector, has freed the pipe. This is a fairly common occurrence and has eliminated many fishing jobs. For example: Drill pipe was stuck at 8340 feet. The Magna-Tector located the stuck point at 6540 feet. However, the Magna-Tector indicated that the pipe was frictionally held by compacted shale or sand. Working the drill pipe loosened the string, freeing it deeper down the well until all the drill pipe was free. The Magna-Tector and immediate action saved the operator many hundreds of dollars.

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# Oil Development in Chile

By John L. Porter

*Technical Consultant*
*Empresa Nacional del Petroleo*
*Member AIME*

***Oil was discovered on the southernmost tip of the South American Continent in 1945. A consultant to the government-owned operating company reviews the numerous problems and progress made in exploitation since that time.***

The oil fields of Chile are in the province of Magallanes, which includes among its geographical features the Strait of Magallanes, the Island of Tierra del Fuego, and Cape Horn.

Punta Arenas, the capital of the province, has a population of 37,000. It lies in latitude 53° South on the Strait of Magellan.

The Magallanes basin which extends from the Cordillera east to, and possibly into the Atlantic and from the Southern part of Tierra del Fuego into Argentina has a maximum sedimentary section in excess of 35,000 ft and covers an area of about 20,000 square miles.[1]

The geology of this basin and the exploratory work there has been described by Thomas[2] and more recently by Mordojovich.[3]

In 1926 the ownership and sole right to develop the oil resources of Chile were taken over by the government.

From 1928 to 1942 the Bureau of Mines was in charge of this work. They did a considerable amount of geological work and drilled several wells, none of which were successful.

In 1942 the work was transferred to the Corporación de Fomento (Corfo), a government owned company whose object is to promote industry in Chile. The Corfo, with the aid of American technical personnel, commenced an active exploration campaign early in 1943.

Oil was discovered in 1945 in the Manantiales Field which lies in Tierra del Fuego on the eastern edge of the Magallanes basin. Production was from the Springhill sand at the base of the sedimentary section. Depth to the sand in this area is 7,500 ft.

Since that time eight more oil or gas fields have been discovered in this area, seven of which — Espora, Angostura, Victoria Sur, Victoria Norte, Chañarcillo, Chañarcillo Sur and Sombrero — are on Tierra del Fuego and one, Punta Delgada, on the mainland.

In 1950 the Empresa Nacional del Petróleo (Enap) was formed as a wholly owned subsidiary of the Corporación de Fomento to administer the country's oil operations. There was no change in company policy or personnel as a result of this move.

The Enap headquarters are in Santiago. Germán Picó Cañas is executive vice-president of Corfo and president of Enap. Fernando Salas is general manager for Enap, with Eduardo Simián as head of production and exploration and Fernando Reich as refinery manager. Osvaldo Wenzel is assistant to Simián in charge of exploration.

Regional headquarters for Magallanes is in Punta Arenas. Enrique Villavicencio is regional manager; Jorge Pacheco, manager of operations and Carlos Mordojovich, manager of exploration.

The organization includes 21 Americans in advisory or supervisory capacities.

The province of Magallanes has no direct land communication with the main part of Chile, and travel for all practical purposes is restricted to boat or plane. It is separated from Puerto Montt, the southern terminus of the Chilean railroad system by nearly 600 miles of mountains and a maze of rugged islands and peninsulas formed by the meeting of foothills of the Cordillera with the Pacific Ocean. This region because of its ruggedness and execrable climate, with high winds, low temperatures and almost continuous rain is practically unin-

FIG. 1 — SEDIMENTARY BASINS AND OIL FIELDS OF SOUTH AMERICA.

habited. Darwin in his class "Voyage of the Beagle" gives an excellent description of this country and its climate.

As the Magallanes basin lies east of the Cordillera there is much less rain fall there and the topography changes from mountains in the west to low rolling hills and typical prairie in the east.

The climate, although better in this area, is disagreeable. The winters are not as cold as in many parts of the U. S., seldom going below 0°F and generally maintaining much higher. In summer, however, the temperature seldom exceeds 60°F. The wind blows almost constantly from October to April. Winds of 40 mph are common and winds up to 100 mph occur at intervals.[4]

The only industry of economic importance in the area outside of the oil operations is sheep raising.

Punta Arenas is not a regular port of call for foreign ships. All materials purchased in the U. S. must be trans-shipped at Valparaíso. Materials must be ordered from six months to a year ahead of need. Almost none of the materials required for oil field work are available locally. A large warehouse stock must be maintained and it must be revised constantly to avoid critical shortages of parts or materials.

The main office, shops and warehouse of Enap are in Punta Arenas, field headquarters for eastern Tierra del Fuego is at Manantiales, small camps for drilling and production personnel are located at Victoria Sur and Sombrero. Each exploratory rig has its own camp.

Transportation of field personnel between Tierra del Fuego and Punta Arenas is largely by plane. A company owned DC-3 makes four flights a week for this purpose while materials are transported by landing craft and truck. The landing craft, while expensive to operate, have proved to be ideal for this work, as they can be landed and unloaded between tides in almost any sheltered beach. They are particularly useful in the Manantiales area because of the very high tides there (40 ft).

The company has had to build and maintain all its principal as well as secondary roads in Tierra del Fuego. There are about 70 miles of main road and equal distances of secondary roads there.

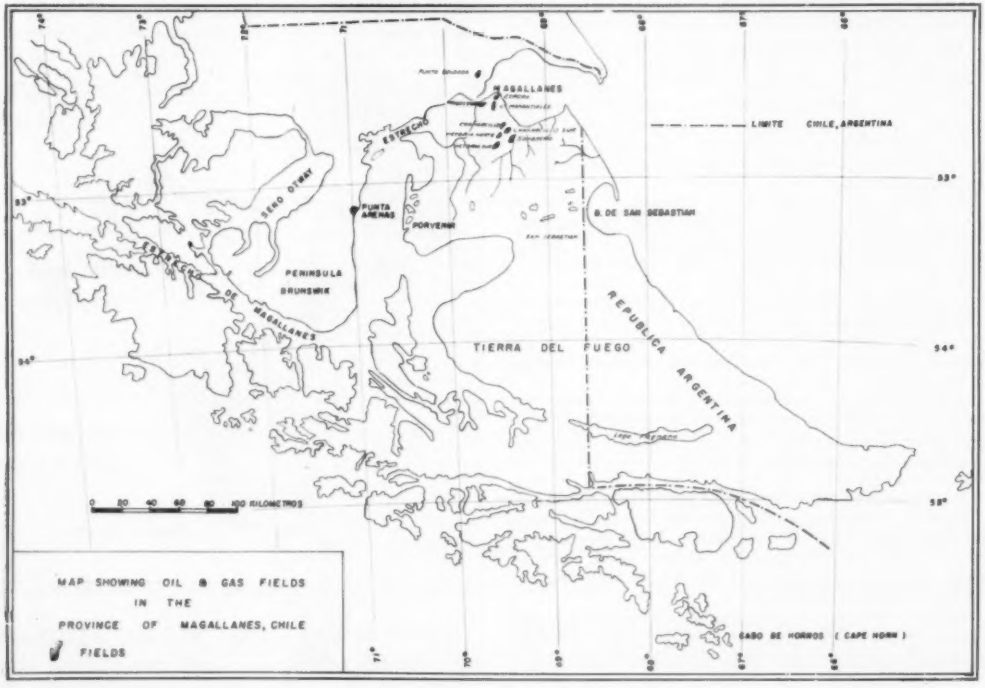
The company has five drilling rigs in operation, two National 100, and three Wilson Titan. Geo. P. Livermore, Inc., has been under contract to furnish technical supervision of the drilling operations since 1945.

In the Springhill sand area no serious drilling problems are encountered. Thirteen and three eighths in. casing is set just below the glacial material at from 100 to 400 ft. In part of the area an artesian water is found at 1,000 ft and some of the wells are drilled with water to 2,000 ft where 9⅝-in. casing is set. Seven and 5½-in. casing is set either through or over the Springhill sand depending on conditions encountered.

The formations as a whole make a fair grade of mud. Caustic soda and quebracho are used for treatment with the addition of bentonites at times to reduce the water loss, and

*Continued on Page 7, Section 2*

FIG. 2 — OIL AND GAS FIELDS IN THE PROVINCE OF MAGALLANES, CHILE.



*Technical Note 140*——

# SOME EFFECTS OF QUICK-FREEZING UPON THE PERMEABILITY AND POROSITY OF OIL WELL CORES

JACOB M. LEBEAUX, THE UNIVERSITY OF TEXAS, AUSTIN, TEX., MEMBER AIME


## ABSTRACT

Oil well cores saturated with water and with water and oil were flash-frozen by immersing the saturated sample in a dry ice-acetone mixture at −82°C. Also, other cores were frozen by direct contact with dry ice alone. Several of the cores fully saturated with water were observed to be completely fractured during the immersion freezing process. The oil-water saturated cores were found to have increased permeability from 4 to 43 per cent after freezing. During the flash-freezing process small needlelike oil particles were seen to be forced out of the core by the expansion which occurred during the freezing process. The permeability of each of the cores was found to have increased after freezing without exception. The authors conclude that rapid freezing tends to increase the permeability and porosity of oil well core samples significantly.

Based on the results obtained, the following equations were derived:

$$k_b = .6967\ k_a^{(1.0296)} \quad \text{(dry ice contact)} \quad . \ . \ . \ . \quad (1)$$

$$k_b = .7044\ k_a^{(1.022)} \quad \text{(immersion freezing)} \quad . \ . \ . \quad (2)$$

where $k_a$ and $k_b$ is the permeability to air after and before freezing respectively.

These equations make possible the prediction of the average change in permeability to be expected when cores are frozen so that appropriate correction of permeability data may be made.


## PROCEDURE

The various samples from oil field cores were cut to 1.8 cm in diameter by two cm in length and were cleaned in carbon tetrachloride and dried in an electric oven. The permeability to air was then determined in the standard manner according to API Code 27. The samples were weighted on an analytical balance, evacuated, and saturated with water. The cores which were to be tested at a liquid content less than 100 per cent saturation, were weighted, and then allowed to stand at atmospheric conditions until part of the water had been lost by evaporation. The percentage saturation was determined by weighing. The cores which were saturated with water and oil were first saturated with water, then partially desaturated by the method described, and then saturated with oil.

The immersion freezing apparatus consisted of a gallon Dewar flask equipped with a tray for raising and lowering the core samples. About four or five inches of acetone was poured in and powdered dry ice added. After approximate equilibrium was attained, as evidenced by a slight bubbling of the carbon dioxide, the core samples were lowered into the mixture and kept there for a minimum period of 15 minutes to insure complete freezing. No attempt was made to measure the temperature of the central part of the core; however, preliminary calculations based on available data showed that five minutes would be ample to lower the temperature of the center of the core to 0°F. After the freezing process, the cores were removed, dried, and the permeability to air again measured.

A second method of freezing employed was to place the saturated cores and dry ice together in the same container for from three to five hours. Again calculations showed that this period was far more than ample to lower the temperature of the core to 0°F. The rate of heat transfer is much faster in the liquid bath than in the dry ice atmosphere.

## DISCUSSION

The first four cores, which were sands from Texas oil fields of unknown origin, were cleaned and completely saturated with water. They were then placed in the dry ice-acetone mixture, which was held at an approximate temperature of −82°C. After a period of approximately five minutes in such a bath

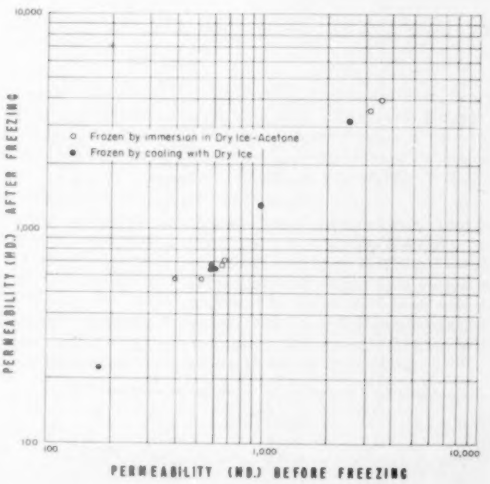



FIG. 1 — THE EFFECT OF FREEZING UPON THE PERMEABILITY OF SOME OIL FIELD CORES.

Manuscript received in the Petroleum Branch office Sept. 25, 1952.

one of the cores split into two separate pieces, so great was the expansion of the water phase in freezing. Another immediately followed suit and within fifteen minutes all four cores had been completely fractured. Other sand cores of lower percentage saturation were frozen by immersion. One rather heterogenous core which had a liquid saturation of 51.6 per cent fractured at the sand-pebble contacts. The permeability to air of all cores after freezing was found to have increased definitely. A core of 52 per cent saturation which did not fracture during freezing nevertheless increased in permeability to air by 7.4 per cent.

A dozen cores with various percentages of water and oil as shown in the accompanying table were frozen either by immersion or contact with dry ice. Although the porosity of all samples was not measured before and after freezing, the porosity of those samples which were analyzed increased significantly (Table I). All cores increased in permeability from 4 to 43 per cent based on the permeability of the unfrozen cores.

Freezing of cores by direct immersion in suitable liquid mixtures resulted in an average increase of 13.5 per cent in permeability whereas the permeability of those cores frozen more slowly in an atmosphere of dry ice increased an average 18.6 per cent.

Research in the frozen food industry has shown the size of ice crystals to be a function of the rate of freezing with slower freezing producing larger ice crystals. The slower rate of freezing with dry ice probably results in the development of larger crystals of water with resultant greater changes in permeability.

Plank[1] has noted that too rapid freezing causes mechanical rupture due to the difference in stress between the internal and external parts. The fracture of all cores completely saturated with water probably is due to the sudden freezing of the outside surface and the subsequent development, as the interior freezes, of internal stresses great enough to result in fracturing.

The following equations:

$$k_b = .6976\ k_a^{(1.0296)} \quad \ldots\ldots\ldots\ldots\ (1)$$

$$k_b = .7044\ k_a^{(1.0226)} \quad \ldots\ldots\ldots\ldots\ (2)$$

are derived from a plot (Fig. 1) of the experimental data in which $k_a$ is the permeability to air after freezing and $k_b$ is the permeability to air before freezing.

Equation (1) is valid for immersion freezing and equation (2) is applicable where dry ice contact freezing is used. These equations may be useful in estimating the permeability to air of cores before freezing.

These experiments were conducted on small core samples. If larger samples were used, it is believed that the permeability change at the center would not be as great as at the boundary, for the water in the center would tend to travel toward the outer boundary and aid in crystal buildup at the outer surfaces, although this speculation should be verified by experiment.

## ACKNOWLEDGMENT

The financial assistance of the Texas Petroleum Research Committee is acknowledged in making this investigation possible.

## REFERENCE

1. Plank, Rudolph: "New Researches on the Preservation of Meat and Fish by the Freezing Process," *Refrigerating Engineering*, (1926), **13**, III-114.

★ ★ ★

**Table I — Effect of Freezing on the Physical Properties of Oil Well Cores**

| Sample | Type Freeze | Saturation Per Cent | Porosity Before | Porosity After | Permeability Before | Permeability After | Change | Fractured |
|---|---|---|---|---|---|---|---|---|
| 1 | I* | 100 | | | | | | |
| 2 | I | 100 | | | | | | |
| 3 | I | 100 | | | | | | |
| 4 | I | 100 | | | | | | |
| 5 | I | | 26.83 | | 137.5 | 191.5 | +39.3 | Fractured during |
| 6 | I | 52.12 | 28.99 | 29.17 | 174.9 | 329.5 | +87.4 | porosity test |
| 7 | I | 53.07 | 24.65 | | | | | Fractured |
| 8 | I | 48.89 | 27.77 | 30.68 | | Fractured in Permeameter | | |
| 9 | I | 48.52 | 28.57 | 30.38 | | Fractured in Permeameter | | |
| 10 | I | 51.60 | 5.39 | 6.63 | Non Permeable | Fractured at sand-pebble contact | | |
| 11 | I | 48.50 | 21.82 | 22.29 | | Fractured in Permeameter | | |
| 12 | I | 45.48 | 9.66 | 11.10 | Non Permeable | | | |
| 13 | I | 32.26 | 21.40 | | 65.5 | 67.42 | | |
| | % Water[1] | | | | | | All +% | |
| 14 | I | 46.26 | | | 677.1 | 702.7 | 3.78 | Average 13.48 |
| 15 | I | 47.85 | | | 327.5 | 353.1 | 7.81 | |
| 16 | I | 52.71 | | | 356.7 | 396.6 | 11.18 | |
| 17 | C** | 51.43 | | | 590.9 | 651.4 | 10.24 | |
| 18 | C | 51.72 | | | 994.6 | 127.6 | 28.29 | 18.57 |
| 19 | C | 47.77 | | | 585.4 | 673.7 | 15.08 | |
| 20 | I | 34.57 | | | 398.2 | 570.2 | 43.19 | |
| 21 | I | 36.14 | | | 653.6 | 687.3 | 5.16 | |
| 22 | I | 32.15 | | | 523.3 | 574.3 | 9.74 | |
| 23 | C | 51.10 | | | 178.1 | 224.1 | 25.83 | |
| 24 | C | 48.93 | | | 254.3 | 319.6 | 25.66 | |
| 25 | C | 31.84 | | | 618.7 | 657.5 | 6.27 | |

*Immersion Freezing
**Contact Freezing
[1]Saturated 100 per cent with water and oil

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# ABSTRACTS — of Papers Presented at the

# First National Conference on Clays and Clay Technology

## *Electrochemical Properties of Clay*

**L. E. Davis**, Department of Soils, University of California, Davis, Calif.

The electrochemical properties of clay are interpreted as related to recent theoretical treatments of ion-selective conductors, *i.e.*, membranes. The analogy with electrodes is considered. Two highly generalized approaches are discussed: (1) Membranes (like electrodes) are phases exhibiting the quasi-thermodynamic properties of junctions (*e.g.*, liquid-liquid junctions); (2) Membranes may to some extent exhibit the characteristics of Gurney-type electrodes as exemplified by Dole's treatment of the glass electrode.

The second approach is considered to be less fruitful at present than the first method of attack. A brief treatment of early ideas is presented. Michaelis' theory is discussed because it has at least one very recent exemplar. Sollner's concepts and researches with perm-selective collodion membranes is discussed with particular emphasis upon his structural interpretation of the phenomena.

A tentative attempt at a critical evaluation of the Teorell-Meyer-Sievers theory is undertaken. Marshall's extensive researches with clay membranes is treated more fully than other experimental work, because (1) Marshall adheres to the Teorell-Meyer-Sievers theory and (2) Marshall used clay in his experiments. The very recent treatment of the non-equilibrium thermodynamics of membrane processes by Staverman is presented. Staverman states that his expression for the membrane potential resembles Michaelis' formula more closely than it does the Meyer-Sievers equation.

An attempt is made to evaluate the impact of these varied concepts upon the implied microscopic characteristics of clay suspensions and gels. The behavior of such systems in relation to the determination of ionic activities is related to the foregoing ideas. No attempt is made at even a partially complete interpretation of the work recently carried out by Jenny, *et al.* However, the results are tentatively discussed in terms of the general theories which have been outlined above.

## *Ion Exchange Reactions of Clays*

**D. R. Lewis**, Shell Oil Co., Houston, Tex.

It has been recognized for many years that many aspects of clay technology including soil treatment and drilling mud treatment must remain in an essentially empirical state until a basis for the understanding of ion exchange reactions is established.

Much of the work on ion exchange reactions of clays in the past has been directed toward establishing total exchange capacities or determining the ionic distribution empirically. This information in general is not suitable for the evaluation of hypotheses designed to provide a basis for understanding the exchange reaction. When the techniques for characterizing the various clay minerals offered the possibility of quantitative study, the solution and exchanger phase contributions to the ionic distribution could be experimentally evaluated in principle. The particular experimental techniques which have been used to measure ionic distribution, however, frequently neglected observations which are essential if the data are to be used for testing and developing theories of ion exchange. It is now well recognized that molecular adsorption, complex ion formation in solution, and ion-pair formation between a mobile solution ion and a fixed exchanger group may occur in addition to the ion exchange reaction. Therefore, if the data are to be useful to develop theories of ion exchange, the whole system must be elected to minimize such extraneous contributions. On the basis of recent theoretical work, various experimental techniques are evaluated from the point of view of their suitability for equilibrium ion distribution studies.

The mass action, adsorption isotherm and Gibbs-Donnan equilibrium formulations of the ion exchange theory are discussed as they may apply to clay systems. Recent progress is summarized in (1) solution thermodynamics of mixed electrolytes as it is relevant to ion exchange processes of clays, (2) the contributions of non-ideality of the clay exchanger phase, and (3) the work of swelling of clays which affects the ionic distributions in ion exchange reactions.

It is concluded that the parameters which relate to the solid phase of the exchanger and those which relate to the solution are now sufficiently well recognized that future experiments can be planned which may more realistically provide an experimental basis for understanding the process of equilibrium ion exchange distributions in aqueous clay-electrolyte systems.

## *Adsorption and Swelling Properties of Clay-Water Systems*

**Isaac Barshad**, Department of Soils, University of California, Berkeley, Calif.

Hydration and swelling in the clays is discussed for three systems: (1) for solid-water vapor systems, (2) for solid-liquid systems at point of gelation, and (3) for solid-liquid systems at points beyond gelations, *i.e.*, in sols.

For the solid-water vapor systems the relation between water adsorption and swelling is most effectively expressed by adsorption isotherms on which the intramicellar swelling is marked. Of greatest interest is data relating to montmorillonite. For this clay the effect of the nature of the exchangeable cation and the total charge on the crystal lattice on hydration and swelling are brought out.

For the solid-liquid systems at point of gelation the relation between swelling and hydration is shown most clearly by the ratio of the liquid to the solid and by the ratio of the volumes of the liquid to that of the dry solid. For the montmorillonites a clear distinction is made between the intramicellar and intermicellar swelling. *X*-ray data indicate that the

**On this and the following pages are abstracts of some of the papers presented at the First National Conference on Clays and Clay Technology, held at the University of California, Berkeley, July 21-25, 1952. The proceedings of the conference, including the full text of each formal paper and the discussion, are to be published at a later date by the State of California Division of Mines. For further information, write Olaf P. Jenkins, Chief of the Division of Mines, Ferry Building, San Francisco, Calif.**

intermicellar swelling is mainly responsible for the macroscopic swelling. The effect of the nature of the adsorbed cations on such swelling is shown for two types of montmorillonites. The possible causes for the variation in the degree of swelling exhibited by different clays is briefly discussed.

For the solid-liquid systems beyond the point of gelation, hydration is of main interest. Viscosity, thixotrophy, and plasticity measurements characterize most suitably such systems. This subject is not discussed in great detail, but it is hoped that it will be taken up in the panel discussion.

The thermodynamics of water adsorption is discussed in relation to the changes which take place in the clay and in the water during the course of adsorption and swelling.

### *Adsorption and Swelling Properties of Clay-Organic Systems*

**Douglas M. C. MacEwan,** Rothamstead Experiment Station, Harpenden, England

This paper is descriptive of methods used and results obtained in the study of interlamellar sorption by montmorillonite and related minerals. Macroscopic swelling is not treated in detail, since the author has not been concerned with work on this subject. The great advantage which the interlamellar complexes of montmorillonite and other minerals present in the study of adsorption is that the standard adsorption data may be checked against X-ray measurements of spacing. Owing to the occurrence of random mixtures of different spacings, however, care must be exercised in making comparisons between spacing measurements and adsorption data.

In favorable cases, information on molecular orientation can be obtained from one-dimensional fourier syntheses. The possibilities and limitations of this method are discussed.

The nature of the forces responsible for interlamellar sorption is discussed in the light of the experimental data.

### *Dye Adsorption as a Clay Identification Method*

**Charles G. Dodd,** Continental Oil Co., Ponca City, Okla.

Dyestuffs and other reagents which exhibit characteristic colors when adsorbed on clay granules have long been employed as aids in clay identification procedures. The colors generally are believed to result from two types of reaction mechanisms. Certain aniline dyes, solutions of which vary in color according to their hydrogen ion content, may be used to indicate the relative acidity of clay surfaces. When clay samples have been pre-treated with acid the color of the adsorbed dye can be correlated with the clay mineral species.

Aromatic diamines, amino phenols, and other compounds which can be oxidized to colored semiquinones permit particularly sensitive and positive identification of members of the montmorillonite family and certain other clay minerals. The nature of this apparently catalytic oxidation on clay surfaces is not understood fully.

The historical development and current applications of these color tests are discussed. Problems encountered in dealing with relatively pure clay minerals, simple mineral mixtures, and complex interlayered lattices are described. The use of para-amino phenol as a new color test reagent is summarized briefly.

### *Infrared Analysis of Clays and Some Associated Minerals*

**Paul G. Nahin,** Union Oil Co. of California, Brea, Calif.

A survey is presented of the theory and practice of the infrared (IR) absorption method for the analysis of clays and related minerals. The information is developed subject-wise rather than chronologically.

Among the topics covered are the following: position of the IR region in the electromagnetic spectrum and origin of the spectra; the path of an IR ray through a spectrometer; demonstration that the different minerals yield different IR spectra, that in contrast to most organic compounds the minerals have fewer absorption bands and in some cases absorb strongly beyond 15 microns; correlation of wavelength, index of refraction, particle size and spectral shape; methods of preparing solid samples; the several absorption bands characterizing different types of water bonding; the bathochromic shift with increasing atomic weight of the cation in carbonate spectra; some tentative IR band assignments; examples of qualitatively and quantitatively useful mineral spectra; use of a template for qualitative analysis and of an optical density vs sample weight working curve for quantitative analysis; an example of IR quantitative analysis of a clay-rock mixture; applications of the method in qualitative analysis of oil field cores.

The review is concluded with a critical assessment of the present status of the field, giving the author's opinion of the directions in which further development appears desirable. To this end, a list of problems is given which it is hoped will excite interest among both academic and industrial research workers in the field of clays and clay technology.

### *Identification by X-ray Diffraction Analysis*

**George W. Brindley,** Department of Physics, Leeds University, Leeds, England

The problem can be usefully considered in relation to the scheme of classification previously described. Since X-ray diffraction patterns are directly related to crystal structures, X-ray identification is, in principal, better suited to the recognition of structural groups and structural varieties than of chemical species.

Well-formed kaolin, mica and chlorite structures give rise to characteristic 7, 10 and 14A spacings which are relatively easily identified. Hydrated forms, such as hydrated halloysite ($d = 10$A) and montmorillonoids under normal conditions ($d = 14$A), are recognized either by low-temperature dehydration giving characteristically diminished spacings, or by the formation of organic complexes giving characteristically increased spacings. This introduces at once the principle that X-ray identification may, and generally does, entail the study of mineral modification by suitable chemical and/or thermal treatment.

The main requirements in the X-ray technique are: (1) Ability to record long spacings up to 25A or even higher values; (2) Well focused lines with good resolution; (3) Absence of back ground scattering and white radiation anomalies. Of these, (1) and (3) lie within the control of the investigator, but (2) depends partly on the material.

The main difficulties of X-ray identification are: (1) The multiplicity of lines when many components are present, and (2) poorly defined diagrams arising from poor crystallinity and/or small size of crystals. The first can be treated experimentally, but the second is inherent in the problem. Simplification of X-ray diagrams is possible by sedimentation, acid treatment and thermal treatment and by the use of orientated specimens. Poor quality powder diagrams (if not due to poor technique) are of interest in themselves and may still give valuable information concerning the clay minerals, more particularly when monomineralic or mainly monomineralic fractions are used. Line profiles give valuable indications of randomly displaced layers and of interstratified sequences.

The recognition of chemical species by X-rays is difficult but some progress can be made if pure or nearly pure specimens are obtainable. The recognition of di- and tri-octahedral

minerals by the (060) spacing is well known but the recognition of micas and chlorites in any greater detail is difficult. A consideration of basal spacings and basal intensities may make more specific identification possible. Results for micas and chlorites will be considered.

## *Electron Microscopy as a Clay Identification Method*

**Thomas F. Bates,** School of Mineral Industries, Pennsylvania State College, State College, Pa.

Electron microscope studies show that most of the clay minerals have morphological characteristics which can be effectively used to aid in their identification. In addition, detailed studies at high magnification have provided structural information not obtainable by others means.

In the kaolinite group each of the common minerals has a clear-cut and diagnostic morphology. However, much more work is needed on flint clays and the kaolins in soils before the same can be said of these varieties. Continued study of halloysite reveals significant details pertinent to the form and structure of the tubular crystals.

Illites from different sources show interesting differences in form which reflect variation in the degree of crystallinity. An illite from the Ordovician Oswego formation shows an unusual development of narrow to broad lath shaped crystals. Except for lower content of iron and magnesium the material has all the characteristics of other illites. The thinnest laths are of the same order of thickness as the flakes of more common illites. Certain mixed layer minerals are identical in morphology with some varieties of illite.

The minerals of the montmorillonite group have been the most difficult of the clay minerals to characterize on the basis of morphology. The lath shaped crystals of certain beidellites, sauconite, nontronite, and hectorite are diagnostic. The metal shadowing technique shows that many of the laths approach one unit cell in thickness.

The morphology of many montmorillonites is dependent upon the mode of sample preparation. The replica method offers a means of studying clay particles in their natural state but this technique is still in the early stages of development as it relates to the clay minerals.

## *Differential Thermal Analysis*

**Richards A. Rowland,** Shell Oil Co., Houston, Tex.

Differential thermal analysis began soon after the development of the thermocouple. It has progressed through the systematic development of better equipment and the cataloguing of typical D.T.A. curves for a variety of materials until good technique now requires control of the composition and pressure of the furnace atmosphere as well as consideration of the thermodynamics and kinetics of the reactions involved. Although differential thermal analyses have been made for many materials, the major applications have been concerned with clay and carbonate minerals.

In D.T.A. curves for clay minerals the low temperature endothermic loop associated with the loss of water and the high temperature exothermic loop, accompanying the formation of new compounds, are changed in shape, temperature and intensity by the kind of exchange cations. The mid-temperature range endothermic loop has a temperature dependence on the partial pressure of water in the furnace atmosphere.

For the anhydrous normal carbonates the dissociation temperature and its dependence on the partial pressure of $CO_2$ are in the decreasing order of *Ca, Mg, Mn, Fe,* and *Zn.* The lower temperature loop of dolomite, the reaction for which must be preceded by an internal rearrangement, is independent of the pressure of $CO_2$ but may be shifted to a lower temperature by prolonged fine grinding which accomplishes a similar rearrangement without involving an activation energy.

A review of the interpretations of D.T.A. curves indicates the necessity for: (1) determining by other methods, usually X-ray, the nature of the product formed by each reaction; (2) establishing whether each thermal loop represents a single change or is a compromise heat effect resulting from several reactions; (3) investigating the effect of varying the gas pressure within the sample to establish the temperature dependence of the reaction on the gas phase. The data from (3) when plotted as van't Hoff lines almost uniquely describe the thermal characteristics of the materials.

## *Clay Technology in Drilling Fluids*

**Delmar H. Larsen,** Consulting Chemical Engineer, Los Angeles, Calif.

In the drilling of oil wells by the rotary process, a circulating mud is used, generally a suspension of clay in water. The clay suspension serves to remove cuttings, and to maintain hydrostatic pressure in the hole. The chief functions of clay in such muds are to impart proper rheological and filtration characteristics. Much of the clay in drilling muds arises from drilled-up formations; but large quantities of surface clays as well as relatively pure clays such as bentonite, attapulgite and others are used. The source, nature and properties of such clays are discussed in some detail. The treatment of clays prior to incorporation in muds is discussed. Various types of chemical treatment of muds, where a change in state of the clay is involved, are discussed, such as the addition of degelling agents, conversion to calcium type mud with protective colloid, salinification, charge reversal, and the like. The use of clays in muds containing oil, both in emulsion muds and oil base muds, is discussed, including the use of organic derivatives of bentonite.

## *The Role of Clay in Oil Reservoirs*

**Norris Johnston,** Petroleum Technologists, Inc., Montebello, Calif.

The history of the consciousness of clay in oil sands as a pertinent and important factor in reservoir behavior is traced. The types of clay and their occurrence are discussed briefly. The microdistribution within the porous medium is shown to have an important bearing on the performance of a reservoir.

The chief effect of clay is the susceptibility to swelling of certain types, with attendant lowering of sand permeability. Other effects of swelling are the resultant sensitivity of sands to volumetric changes affecting production history, land subsidence, laboratory test procedures, and the increase of irreducible interstitial water content relative to a clean sand of similar non-swelling matrix. Other effects are a possibly greater water wettability, and the greater ion adsorption on clay surfaces than on silica and other less active surfaces, which alters the electric log characteristics.

Means are described for counteracting certain of the worst characteristics, and taking advantage of other aspects of the clay effects. Certain views on micro-distribution are presented in an attempt to explain observed physical properties of argillaceous and clean sands.

Some likely trends of future research are suggested.

## *Clay Technology in Well Log Interpretation*

**M. R. J. Wyllie,** Gulf Research and Development Co., Pittsburgh, Pa.

The electrochemistry of the shale cell in the earth is examined in the light of modern electrochemical theories of charged membranes. It is shown that a consistent shale baseline on an SP log appears to indicate that shales, when subjected to

*Continued on Page 4, Section 2*

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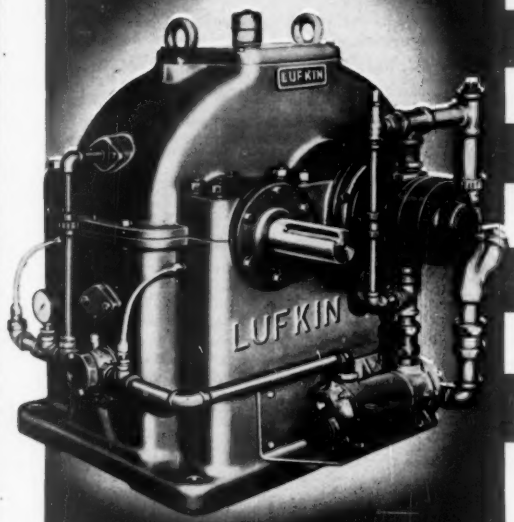


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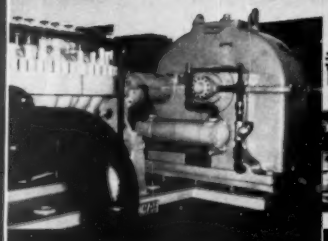

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# Petroleum Reservoir Mechanics

Reported by J. A. Klotz

*Pacific Technology Forum*

William T. Cardwell, Jr., senior research engineer for the California Research Corp. and past chairman of the Pacific Technology Forum, continued the series on the "Elements of Petroleum Production." Cardwell, the sixth speaker in the series of ten, talked about petroleum reservoir mechanics; the remaining four speakers will discuss solution gas drive, gravity drainage, natural water drive, and condensate production.

Cardwell emphasized the elements and first principles of fluid flow in petroleum reservoirs. These first principles may seem to be of little interest to anyone who has passed the beginner stage of reservoir engineering, but even "authorities" on this subject benefit when these fundamentals are again reviewed. A review of fundamentals of fluid flow reminds engineers of the large background of experience and empiricism that lies between these fundamentals and the art of oil field reservoir engineering. Although universally applicable, quantitative laws that can be used by petroleum engineers cannot be stated, a few fundamentals that we know to be true about fluid flow can be stated. These fundamentals keep intuition strong and minimize erroneous thinking.

The quantity of liquid flowing through a porous block cannot be calculated from fundamentals as can the quantity of liquid flowing through a smooth capillary. Intuition that results from analysis of flow through the capillary tells us, however, that flow through the porous block must be proportional to the pressure difference across the block, $P$, and to the area of the block, $A$, and inversely proportional to the liquid viscosity, $\mu$, and to the length, $L$, of the block. This intuition can be validated by experimental measurement, which shows that

$$Q = \frac{K \cdot A \cdot P}{\mu \cdot L}$$

$K$ is a true empirical factor, its value cannot be determined except by measurement of the other terms. In the art of reservoir engineering this equation is known as Darcy's law and the factor $K$ is known as the rock permeability.

Darcy's law for the flow of fluids through porous media is similar to laws in other branches of science that on first view appear far removed from reservoir engineering. Ohm's law of the flow of electricity, Fick's diffusion law, Fourier's law of heat conduction, as well as Darcy's law, all may be written in the following form:

flow rate = conductivity x potential gradient

These laws are a basis for the application of the mathematics of potential fields to electrical problems, or diffusion problems, or heat conduction problems or flow problems. Thus petroleum engineers may draw on a large background of information that has been accumulated about potential field problems arising in other branches of science. The solutions to many of these problems have been translated into reservoir engineering terminology by Muskat.[1]

One of the most useful formulas that can be derived readily from Darcy's law is the radial flow formula,

$$Q = \frac{2\pi khp}{\mu \log_e (r_e/r_w)}$$

This equation relates the flow, $Q$, into a well of radius $r_w$ from a cylindrical drainage circle of radius $r_e$, to $k$, the Darcy's law constant (the permeability of the formation); $h$, the thickness of the formation; $P$, the difference between the fluid pressures at the drainage circle and at the well bore; and $\mu$, the viscosity of the fluid. This equation is similar to the Darcy's law equation except that the term expressing the size of the system, $L$ in the Darcy equaion, is here a logarithmic term. Whereas flow predicted by the Darcy equation changes in the same proportion that $L$ changes, the flow predicted by the radial flow formula changes only as the logarithm of $r_e/r_w$.

Equations, such as this radial flow formula, are far too simple to predict the flow of oil into a well. Once this flow has been measured, however, these equations often can be used to show whether or not the flow can be changed. For example, intuition tells us that production could be increased if the well radius, $r_w$, could be enlarged. The radial flow equation shows that intuition is qualitatively correct, but that a well radius enlargement to about 12 ft would be required to double the oil flow rate. Tthus, this method for increasing production is entirely impractical.

A reservoir engineer interested in well completion effectiveness, or in the effect on production of changing the permeability of the formation near the well bore can derive the following equation from the radial flow formula:

$$Q = \frac{2\pi hP}{\mu\left[\frac{1}{k_1}\log_e (r_1/r_w) + \frac{1}{k_2}\log_e (r_e/r_1)\right]}$$

Like the radial flow formula, this equation is too simple to predict the flow of oil into a well, but the equation shows that production is more sensitive to a change in the permeability, $k_1$, near the well bore (between $r_1$ and $r_w$) than to changes in permeability between $r_1$ and $r_e$. The change in production is not, however, proportional to the change in permeability near the well bore. For example, if this permeability changes by 90 per cent, production may change by only 20 per cent. The equation also tells that laboratory data showing permeability damage to short cores cannot be applied directly to show productivity damage to wells.

If the petroleum engineer has at his disposal mathematics that are more powerful than those used to derive the radial flow formula, he can derive the following equation which will give him information about flow into a well that is partly blocked, such as by a perforated liner cemented in place or by mud cake, impermeable except through specific openings:

$$Q = \frac{2\pi khP}{\mu[\log_e (r_e/r_w) + (2/n)\log_e (2/\pi a)]}$$

In this equation, $n$ is the number of rows of holes in the sheath that lines the well and $a$ is the fraction of the bore face area that is open for flow. This equation shows that production depends not so much on the fraction of well bore face area that is open as on the number of rows of slots. If data representing a particular field well are inserted into this formula, the reservoir engineer discovers that, as long as $a$ is greater than about two per cent, the well's production cannot be in-

*Continued on Page 4, Section 2*

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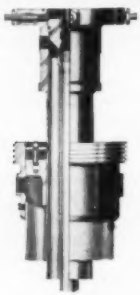

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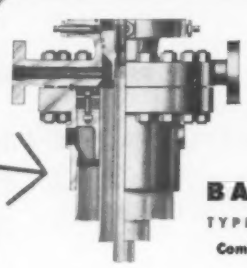

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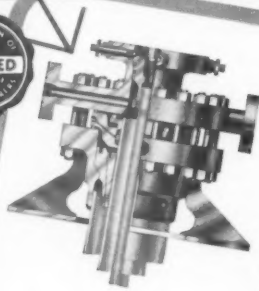

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# *A HIGH-PRESSURE WELLHEAD LUBRICATOR*

**HOWARD E. McKINNEY**, SHELL OIL CO., HOUSTON, TEX.

## ABSTRACT

A high-pressure wellhead lubricator has been developed to facilitate telemetering electrical measurements from subsurface reservoirs to the surface with the well under normal flowing conditions.

The field unit in use at the present time employs a 5/16-in.-diameter, single-conductor armored cable and is to be used in wells with surface pressures up to 5,000 psi. It has a pressure sealing element that maintains a continuous and absolute seal around the cable as it enters or leaves the tubing at speeds up to 175 ft per minute. A cable injecting device is used which obviates sinker bars or weight sections on the instrument.

## INTRODUCTION

The development of instruments for securing physical measurements in pressure wells has been confined in the past to those instruments which would operate on a wire line and record the necessary measurements in the downhole instrument itself, or those which would operate on an electric cable in a well with the surface pressure killed by the use of weighted fluids or by the use of tubing plugs. In one case the accuracy of the measurements is questionable, and in the other the range of application is very limited.

Considerable work has been done by other interests to provide effective means to accomplish the necessary telemetering. The U. S. Bureau of Mines developed a wellhead lubricator prior to 1947 which permitted a 5/16-in.-diameter single-conductor cable to be lowered into a well with a surface pressure of approximately 500 psi. This unit was used successfully in a number of tests in Oklahoma. A company which tests wells has recently offered on a service basis a wellhead lubricator with a 3/16-in.-diameter cable that reportedly operates up to 2,500 psi surface pressures. Each of the above operates on a staging principle to effect a seal. In both of these units some leakage of well fluid occurs when the cable is moved.

Manuscript received in the Petroleum Branch office July 29, 1952. Paper presented at the Petroleum Branch Fall Meeting in Houston, Tex., Oct. 1-3, 1952.

## SPECIFICATIONS FOR DESIGN

In order to provide the maximum flexibility in its use, the following parameters were established for the design of our high-pressure wellhead lubricator:

1. An absolute well fluid seal up to 5,000 psi surface pressures.
2. Means for raising and lowering the instrument at speeds of at least 100 ft per minute.
3. Provision for the instrument to enter and leave the well without disturbing the well flow or the reservoir conditions.
4. A cable large enough to provide suitable electrical characteristics and suitable mechanical properties.
5. A method of operation that will not damage the well in any way.

The present high-pressure wellhead lubricator field unit fulfills the above requirements.

## DESCRIPTION OF THE UNIT AND ITS OPERATION

The cable selected for this use is the standard Amergraph 1H2 as manufactured by the American Steel and Wire Co. This particular cable is normally used by the Halliburton Oil Well Cementing Co. in their conventional well logging operations. Although the cable presents a noncircular cross-section (Fig. 1), its diameter is very consistent; for example, maximum diameter is 0.325 in., minimum diameter 0.314 in. This factor permits the use of the sealing element, as later described.

Early in the development of the high-pressure wellhead lubricator it was apparent that we could not effect a direct gas seal around a moving 1H2 cable. This becomes evident when an examination of the cable cross-section is made. The voids between the strands of the outer armor provide natural channels for the flow and escape in large quantities of a low-viscosity fluid such as gas. However, it is relatively simple to

effect a seal around the moving cable when a viscid fluid (transfer fluid) of our own choosing, rather than gas, is used in the pressure chamber. Sealing is achieved in our field unit by this indirect method. The sealing element is so designed that the cable can enter the well only through a relatively long, small-diameter tube, providing a very small cross-sectional area (annular space) for the well pressure to act upon, and sufficient length that the cylindrical shear area of the transfer fluid is large enough to permit only a very low rate of flow of the transfer fluid through the sleeve. A continuous supply of transfer fluid is injected into the sleeve a few inches downstream from the well-fluid chamber. Since the pressure of the transfer fluid is well-pressure plus 200 psi, the fluid tends to flow in both directions from its entry port; that is, towards the well fluid chamber and towards the atmosphere, thus preventing the well fluid's escape.

The cross-sectional area of the annulus between the cable and the sleeve is 0.003 sq in. There is approximately 0.016 sq in. of void area in the cable itself, giving a total well-fluid force area of only 0.019 sq in. Thus, in a well with 5,000 psi surface pressure, only 95.5 lb are actually applied to force the transfer fluid out of the sleeve. A sleeve 18 in. long provides ample cylindrical shear area so that a very low flow rate occurs at this pressure.

A sealing sleeve of the above type was constructed and subjected to rigorous bench and field testing prior to its assembly in a field unit. At the time this testing was proceeding, considerable effort was made to select a transfer fluid that had suitable rheologic properties and, at the same time, met the requirements of noncorrosiveness, proper solubility in well fluids, temperature stability, availability, and economy. The transfer fluid selected for use was Shell Indus 5169 grease.

The sealing element of the field unit offers very little drag to resist cable movement. However, when a cable with a diameter of 5/16 in. is placed in a pressure chamber, a considerable force (80 lb per thousand psi well pressure) acts to extrude the cable from the chamber. This force must be overcome with a counterforce that acts to pull the cable into the pressure chamber before entry can be made. The use of sinker bars on the bottom of the instrument is not practical with a 5/16-in.-diameter cable, since more than 66 ft of 1½-in.-diameter bars are required to lower an instrument into a 5,000-psi well with two-in. tubing. A cable cannot be pushed in from the outside, as a compression force of only 100 lb on a one-in. section of cable will cause basketing in the outer strands. Hence, it has become necessary to devise a method of pulling the cable into the well from inside the pressure area itself. This is accomplished in the field unit by use of a grooved sheave. The groove in the sheave is essentially a half circle of slightly smaller diameter than the cable diameter. The gripping action of the groove is further increased by employing rollers that push the cable more tightly into the groove. As the cable is forced into the groove, the whole sheave is turned, thereby providing a continuous pull on the cable from the pressure chamber. As this entire cable injector assembly is operated at well pressure or greater, its design along conventional lines would result in a very heavy and cumbersome apparatus. By removing the center portion of the assembly, a modified torus ring is formed which materially decreases the wall thickness required for the pressure housing.

Details of the unit are shown in Fig. 2. The instrument, normally 1¼-in. diameter and five-ft long, is shown in the lubricator section. The cable head is designed to connect the cable mechanically and electrically to the instrument. Although the cable has a rated breaking strength of 9,200 lb, the mechanical connections to the cable head are made to provide a weak connection of 3,000 lb pullout so as to insure that the cable will pull free from an instrument stuck in the hole. The cable from the well side leaves the instrument to pass into the instrument catcher assembly. This is a safety feature to be used in case the instrument, as it is being brought up hole, is not stopped at the top of the lubricator. In this event the head of the instrument will hit a plug and shear two pins, thus allowing the spring fingers to grab the instrument as the cable is pulled from the weak link in the head. The cable goes next into the cable cutter assembly. This device can be used to cut the cable and allow it to fall clear of the master valve on the wellhead. The conditions requiring severing the cable will occur very infrequently, if ever. However, severing the cable could permit the well to be shut in at the wellhead, even though the instrument and a section of cable would remain at the bottom of the tubing.

The cable goes next through the cable brake assembly. This unit may be used to govern the uphole speed of the instrument. It is actuated by forcing high-pressure hydraulic fluid from an external source into the annulus around the rubber-like sleeve causing it to press steel brake shoes against the cable.

The next section is a cable valve, or stationary cable seal. This unit is physically the same as a cable brake except that it has no shoes. The neoprene sleeve is pressed directly into the outer strands of the stationary cable to effect a seal. Transfer fluid is injected into this seal to fill the inner voids

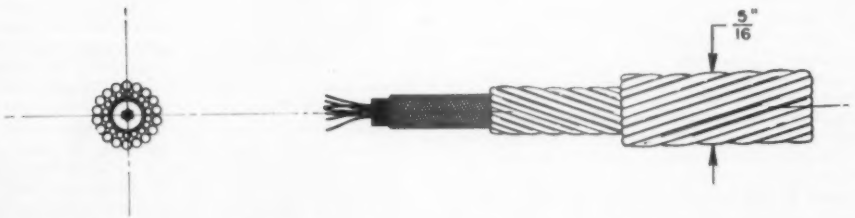


FIG. 1 — AMERGRAPH 1 H 2 SINGLE CONDUCTOR ARMORED CABLE.

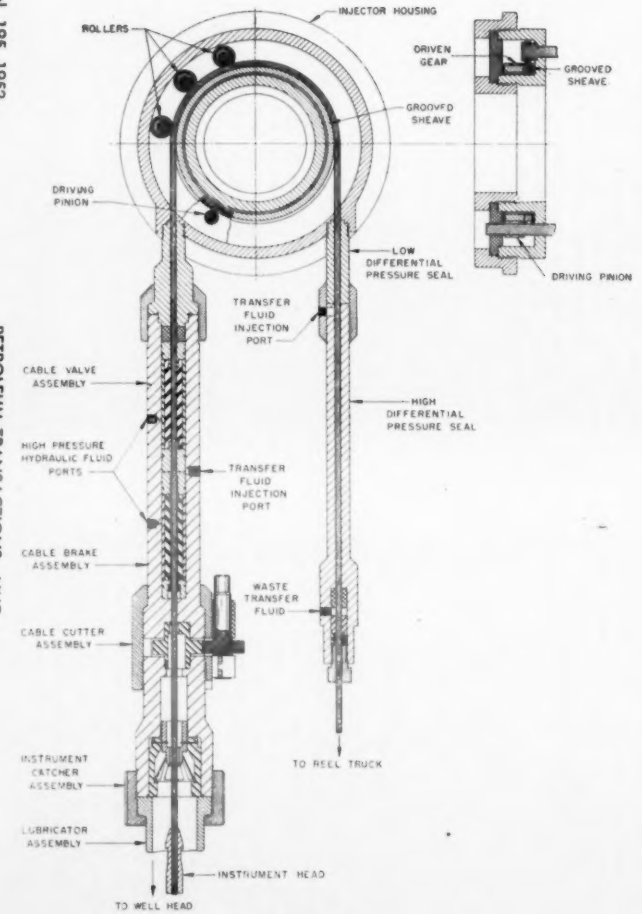


FIG. 2 — HIGH PRESSURE LUBRICATOR.

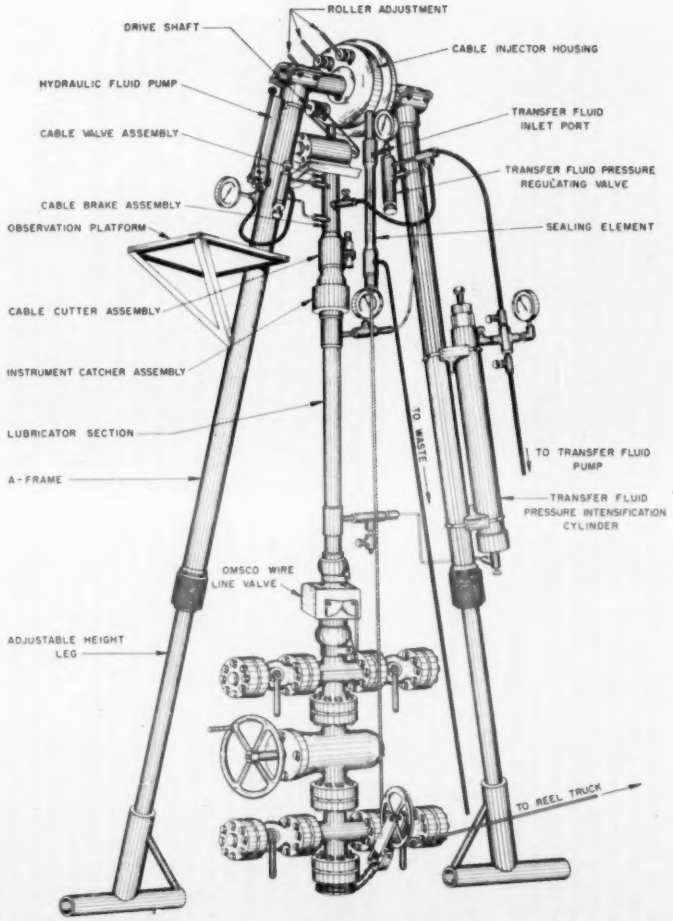


FIG. 3 — FIELD UNIT ASSEMBLY.

of the cable. It is used when it is necessary for the instrument to stay in one place for a long period of time, for example, in securing bottom-hole pressure-build-up data. The cable next enters the injector where it goes around the sheave and under the pressure wheels. The pressure wheels are not normally required, as the gripping action of the sheave is ample for most well pressures. The injector sheave is rotated in either direction by an externally located explosion-proof electric motor.

The cable next passes into the low differential pressure portion of the sealing element, past the transfer fluid injection port, through the high differential pressure portion of the sealing element, and then out of the sealing element to the reel truck.

Fig. 3 shows the general layout of all the components as they are assembled over a well. The wellhead equipment is mounted on and supported by an *A*-frame adjustable in height to facilitate connection to most Xmas trees. This frame, when connected to the Xmas tree, forms a rigid tripod with the lubricator section or instrument chamber acting as the third leg. This assembly is designed to support safely a pull in excess of the cable strength of 9,200 lb. The complete unit is designed to work at well pressures up to 5,000 psi; it incorporates a reel truck with 12,000 ft of the 5/16-in. single-conductor cable. The field unit can be assembled over a well in approximately four hours. A reduction in this time is anticipated in the future. Normally three men are required to operate the complete unit and the reel truck. Fig. 3 also shows the transfer-fluid pressure-intensification cylinder. This unit is a piston and cylinder arrangement from which a supply of transfer fluid is available for injection at a given pressure above well pressure. It takes care of sudden fluctuations in well pressure and acts as a high-pressure transfer-fluid reserve.

The amount of transfer fluid used in a normal well is approximately two lb per thousand ft of cable. The sealing element uses approximately 0.02 lb per minute per thousand psi wellhead pressure when the cable is stationary. For a moving cable the transfer-fluid requirement is almost independent of the well pressure and of the cable speed. The quantity of transfer fluid used is approximately that required to fill the voids in the cable, and since it is dissolved by the well fluid, the transfer fluid must actually fill the voids both going in and coming out of the well.

## TESTS OF THE UNIT

Tests have been made where the packing element was deliberately made to fail by stopping the transfer fluid pump which allowed the well gas to enter and flow through the sealing element. At 5,750 psi wellhead gas pressure, the flow of gas was quite hard, but was easily stopped within ten seconds after the transfer fluid pump was started. Usually one stroke of the transfer fluid pump (0.016 lb of transfer fluid) is sufficient to stop the flow of gas and regain an absolute seal about the cable.

The well service unit has been bench-tested to 8,700 psi, thoroughly field-tested at well pressures up to 3,060 psi, and mock-tested at gas pressures of 5,750 psi. The unit is presently being utilized to run into pressured wells the several electrical telemetering instruments being developed at the laboratory. To date the field unit has logged an accumulated cable travel of over 115,000 ft.

The design and development of the unit will continue with the hope that the high-pressure electrical cable service can be made generally available to the field. ★ ★ ★

# X-RAY SHADOWGRAPH STUDIES OF AREAL SWEEPOUT EFFICIENCIES

R. L. SLOBOD, MEMBER AIME, AND B. H. CAUDLE, JUNIOR MEMBER AIME, THE ATLANTIC REFINING CO., DALLAS, TEX.

## ABSTRACT

In the past, the main emphasis in attacking the problem of the recovery of oil has been on the determination of fluid flow characteristics and residual oil saturation in the part of the reservoir which is contacted by a displacing phase. It is recognized that the determination of the fraction of the reservoir contacted in secondary recovery operations is also of great importance in predicting the ultimate recovery to be expected. A method is described in which radiographic techniques are used to determine these areal sweepout factors for any type of well spacing. Data showing the relationship of viscosity ratio and relative permeability to areal sweepout efficiency are presented for the five spot and the direct line drive well spacing patterns. Further applications of the method to studies of the displacement efficiency in the area contacted are mentioned.

## INTRODUCTION

The problem of increasing oil recovery from typical reservoirs is generally attacked by trying to devise some means for reducing the residual oil in that part of the reservoir which is contacted. The fraction of the reservoir contacted in the displacement process, however, is also of major importance but has been given less consideration in the past. One reason for this neglect is the meager information available on the portion of the reservoir contacted and the magnitude of changes in this factor as operating conditions are varied. Until recently, the only means available for determining this quantity has involved the use of the electrolytic or potentiometric models[1] in which one is limited to working with a mobility ratio of unity. While means for calculating the volume of a reservoir contacted do exist, the calculations are very tedious for systems with mobility ratio different from unity. Recently several such determinations have been reported,[2,3] and an experimental method involving a step-wise use of potentiometric models has been described.[2]

A new method which has been developed for studying the areal distribution of phases in a porous medium is discussed below. This tool can be used to determine the effect of operating variables such as viscosity, relative permeability, presence of gas, mobility ratio, rate and stratification on the fraction of the reservoir contacted by the displacing medium. This development based on the use of *X*-rays gives a pictorial representation of the location of the phases. Further, the amount of each phase at each point of interest can be determined quantitatively.

## X-RAY METHOD FOR AREAL STUDIES

In this method the location of various phases distributed over a test area are observed simultaneously by obtaining a photographic record of the transmission of *X*-rays through the test plate. This procedure is an adaptation of the radiographic techniques which have long been used in the medical and industrial fields. Just as the medical profession uses a chest plate to show spatial interrelationships, the location of an *X*-ray absorbing fluid and a nonabsorbing fluid in a porous medium can be determined by obtaining a photographic record of transmitted *X*-rays. Moreover, as changes occur in such a system, these changes can be observed by taking successive photographs. Previously,[2] *X*-ray methods have been used in fluid flow studies to determine quantitatively the saturation at a given point in the system. The intensity of the transmitted *X*-rays was measured by an ionization chamber, so that a point by point survey of saturation could be made. In comparison with this earlier quantitative procedure, the photographic procedure which simultaneously observes the saturation at many

[1]References given at end of paper.

Manuscript received in the Petroleum Branch office July 31, 1952. Paper presented at the Petroleum Branch Fall Meeting in Houston, Tex., Oct. 1-3, 1952.

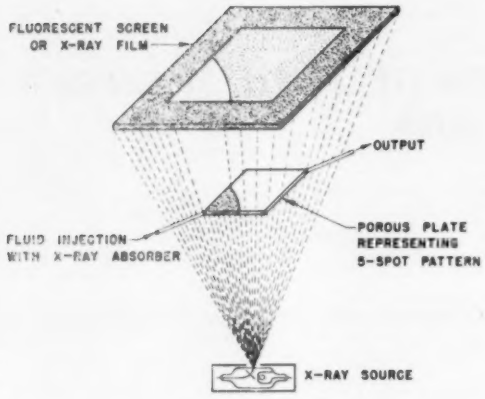


FIG. 1 — X-RAY APPARATUS FOR STUDYING AREAL SWEEPOUT PATTERN.

points obviously lends itself to studying areal effects, particularly when changes are taking place rather rapidly.

The radiographic technique is particularly applicable to the study of samples of uniform thickness. In practice, such a plate is saturated with one phase and displaced with a second — one of the two phases containing the $X$-ray absorbing material (iodobenzene, potassium iodide, etc.). A uniform field of $X$-rays is directed against one face of the plate, and a photographic film is mounted behind the plate to record the transmitted $X$-rays. In this manner those portions of the film directly behind a portion of the sample rich in $X$-ray absorping fluid will remain essentially unexposed while the other portions of the film where $X$-rays have penetrated will be darkened. The developed plate, therefore, shows the relative position of the phases in the area studied. The size of the sample which may be investigated with a single exposure is limited only by the area of the uniform $X$-ray field and the dimensions of available film.

## Quantitative Determination of Saturations From Film Density

Quantitative saturation data at any point in the porous plate being studied may be obtained by utilizing the linear relationship between the optical density of the developed radiograph and the concentration of $X$-ray absorbing matter in the path of the $X$-ray beam. This relationship can be derived from a consideration of Lambert's Law and the sensitometric characteristics of $X$-ray films.[5]

Thus:

$$\frac{I_t}{I_o} = e^{-kx} \text{ — Lambert's Law} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{or } \log \frac{I_t}{I_o} = -kx \log e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where:

$I_o$ = Intensity of the incident $X$-ray beam
$I_t$ = Intensity of the transmitted $X$-ray beam
$k$ = absorption coefficient
$x$ = thickness of the material
$\rho$ = saturation of the $X$-ray absorbing material
$E$ = relative exposure of the photographic film
$D$ = optical density of the developed radiograph

In a porous plate of uniform thickness with an $X$-ray absorbing fluid in one of the fluids present, $-k \log e$ is constant and the thickness of the absorbing material is directly proportional to the saturation of the $X$-ray absorbing fluid in the porous medium. Therefore:

$$\log \frac{I_t}{I_o} = K\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since $\frac{I_t}{I_o}$ is the relative exposure, $E$, given the radiograph:

$$\log E = K\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The relationship between the original exposure and the optical density of the developed radiograph is given by the characteristic curve for the film being used. If the film chosen exhibits a linear relationship between $\log E$ and density (as does Eastman Blue Brand $X$-ray film) then:

$$D = K'\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

for the density interval in which the characteristic curve is a straight line.

Since small differences in either exposure or development change the exact relationship given in equation (5), the step-wedge is included in each radiograph taken. This step-wedge is constructed of aluminum to have, on one end, the same $X$-ray absorptive capacity as the unsaturated plate and, on the other end, the absorptive capacity of the plate fully saturated with the phase containing the tracer. By these means, the relationship between density and saturation may be determined experimentally for each radiograph taken.

Saturation values obtained by this method have been found experimentally to be accurate to well within plus or minus

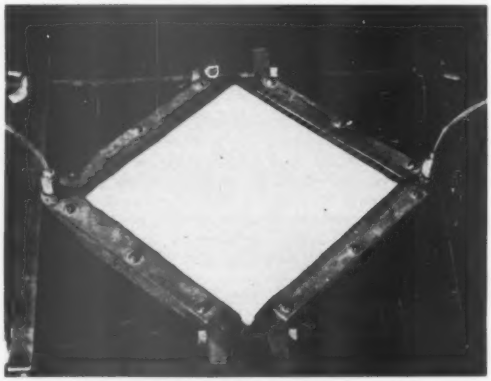

FIG. 2 — POROUS PLATE ASSEMBLY FOR STUDYING FIVE-SPOT FLOODING PATTERNS.

FIG. 3 — TYPICAL RADIOGRAPH SHOWING AREAL SWEEPOUT EFFICIENCY FOR THE FIVE-SPOT WELL SPACING. MOBILITY RATIO = 1.

five per cent of the pore volume, and on a given photographic plate saturation differences of one per cent of the pore volume may be detected.

## EQUIPMENT, MATERIALS AND PROCEDURE

The *X*-ray source used was a Westinghouse medical unit rated for 80 kilovolts and 30 milliamperes. The apparatus was arranged as shown in Fig. 1. The *X*-ray beam was directed vertically through the sample under study to the fluoroscopic screen or *X*-ray film, and the entire apparatus was suitably enclosed in lead shielding to protect the operator from stray radiation.

The porous media used in the study were of fused Alundum (made by the Norton Co., Worcester, Mass.) fabricated in plate form with a thickness of ¼ in. These plates, when cut to the correct dimensions for the well spacing pattern to be studied, were placed in metal holders with rubber gaskets as shown in Fig. 2. All remaining exposed surfaces had been sealed with a ceramic type glaze fused onto the Alundum surface at 2,000°F. (This is a sodium borosilicate glaze containing small amounts of potassium, calcium and aluminum.) Fluids were carried to and from wells in metal fittings which projected through the gaskets.

When the oil phase was selected to absorb *X*-rays, iodobenzene in concentrations up to 50 per cent by volume was added to a pure hydrocarbon to give the desired absorption of *X*-rays. Similarly, a solution of potassium iodide in distilled water (Sp. Gr.-1.5) was used when it was more desirable to make the water phase the *X*-ray absorber.

Eastman Kodak Blue Brand Medical *X*-ray Film, because of its favorable characteristic curve, was used with calcium tungstate intensifying screens to record the shadowgraph patterns produced. With the *X*-ray source at a distance of 30 in. from the film, an exposure of ½ second at five milliamperes and 56 kilovolts was found to produce radiographs with a satisfactory range of densities. The film was developed in accordance with the manufacturer's recommendation. With this technique radiographs such as the one shown in Fig. 3 were obtained.

## AREAL SWEEPOUT EFFICIENCIES FOR A FIVE-SPOT WELL SPACING

Areal sweepout patterns which have been obtained in earlier studies have shown that the area swept at breakthrough for a five-spot well spacing is 72 per cent. A listing of both published and unpublished results of sweep efficiencies in the five-spot pattern for unit mobility ratio is as follows:

| | |
|---|---|
| a. Muskat (early electrolytic method)[3] | 75±3% |
| b. Muskat (early analytical solution)[7] | 72.3% |
| c. Hurst (analytical solution)[8] | 72.6% |
| d. Muskat (later analytical solution)[7] | 71.5% |
| e. Fay and Prats (numerical solution)[9] | 73 % |
| f. Aronofsky (unpublished potentiometric results) | 70 % |
| Average | 72.2% |

These results would apply in a system in which no capillary forces are acting, the displacement efficiency of the flood is 100 per cent, and the viscosity ratio is unity. It was believed that reproducing these conditions using the *X*-ray shadowgraph technique should give the same areal sweepout pattern and thus serve as a calibration of the newer method.

The square plate shown in Fig. 2 which represents one section of a five-spot pattern was saturated with a non-*X*-ray absorbing oil which was then displaced at a constant rate with an *X*-ray absorbing oil of the same viscosity. The two fluids were miscible in all proportions. The *X*-ray shadowgraph obtained at the time of breakthrough is shown in Fig. 3. The area swept at breakthrough was 69 per cent. These results

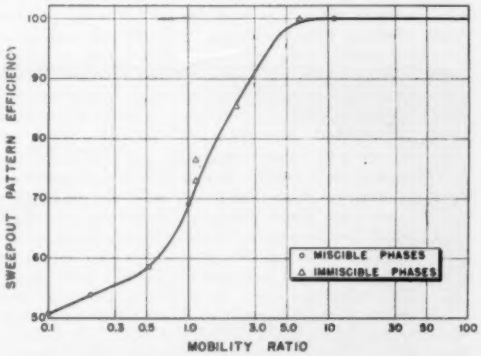


FIG. 4 — SWEEPOUT PATTERN EFFICIENCY *VS.* MOBILITY RATIO FOR THE FIVE-SPOT WELL SPACING.

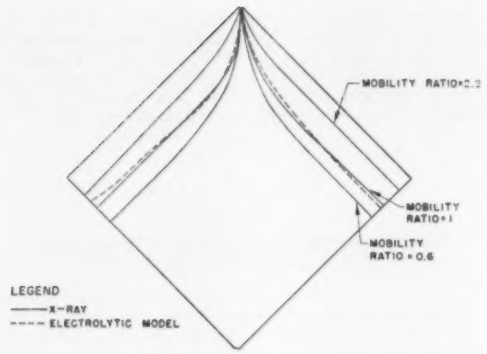


FIG. 5 — AREAL SWEEPOUT PATTERNS, FIVE-SPOT WELL SPACING

indicated that at the only checking point available the potentiometric model and the *X*-ray technique were in good agreement.

It has been previously established that the areal sweep efficiency is markedly dependent upon the mobility ratio

$$M = \frac{k/\mu \text{ (ahead of the front)}^2}{k/\mu \text{ (behind the front)}}$$

rather than upon the viscosity ratio alone. In the special case where the injected fluid is miscible with the produced fluid the permeabilities ahead of and behind the front are equal and

$$M = \frac{\mu \text{ (behind the front)}}{\mu \text{ (ahead of the front)}}$$

When the miscible fluids used have equal viscosities the mobility ratio is one, and by varying the viscosities of the fluids other mobility ratios may be studied.

Using miscible phases of varying viscosity ratios, areal sweepout efficiencies for the five-spot pattern were determined for mobility ratios between 0.1 and 11.0. The data obtained are shown by the circles plotted in Fig. 4. The curve drawn through these data portrays the effect of mobility ratio on the areal sweepout efficiency at breakthrough of the injected fluid. Areal sweepout efficiencies range from 50 per cent at unfavorable mobility ratios of 0.1 to 100 per cent at mobility ratios of six or better. In the range of mobility ratios between one and three — in which a large number of field water floods fall — substantial benefits in sweepout pattern efficiency can result from moderate increases in mobility ratio.

In order to verify experimentally the role of mobility ratio as determined from relative permeability measurements on the areal efficiency of the test flood, water was injected into the five-spot plate which contained oil and connate water. From the relative permeability curves for the porous material being used, and the average saturation behind the water front, the mobility ratios were determined to be 1.14, 2.15, and 6.2. Two experiments were done at 1.14 mobility ratio. Areal sweepout efficiencies observed for these calculated mobility ratios are also shown in Fig. 4. It may be seen that these data agree within experimental error with the results obtained when miscible phases were used. It should be realized that there is a possible source of error in the relative permeability data used which were determined on a core plug of similar material. It is felt that the agreement between the two types of displacement studies offers proof of the role of permeability as a factor in determining area sweepout efficiencies. The agreement in these data has also been interpreted as providing justification for the use of miscible phase displacements to determine the effect of mobility ratio on areal sweepout efficiencies.

Typical five-spot breakthrough patterns for a range of mobility ratios are shown in Fig. 5, together with the areal sweepout efficiency for a mobility ratio of one as obtained from electrolytic model studies.[3] It may be seen that the breakthrough pattern for a mobility ratio of one, which was obtained using miscible phases, corresponds closely to that predicted by the electrolytic model.

## AREAL SWEEPOUT EFFICIENCIES FOR A STRAIGHT LINE DRIVE

The technique of using miscible phases at various viscosity ratios was also used to study the effect of mobility ratio on areal sweepout efficiencies for a straight line drive type of well spacing in which the ratio of the distance from injection well to producing well to the distance between injection wells is 1.5:1. (Same ratio as used in Reference 2.) Sweepout pattern efficiencies were determined for mobility ratio values from 0.25 to 8.3. Results of these experiments are shown in Fig. 6. The value of 68 per cent areal sweepout efficiency obtained at a mobility ratio of one is considered to be experimental verification of the 71 per cent value estimated from mathematical analyses and electrolytic model studies. A listing of available data on the sweep efficiency for unit mobility ratio for the straight line drive pattern is as follows:

| | |
|---|---|
| a. Muskat (analytical solution)[1] | 70.5% |
| b. Aronofsky (numerical solution)[2] | 70.0% |
| c. Aronofsky (potentiometric method)[2] | 71.6% |
| Average | 70.7% |

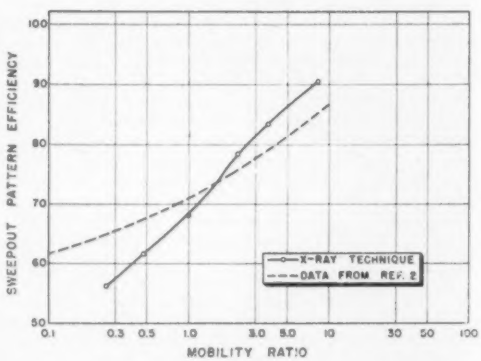


FIG. 6 — SWEEPOUT PATTERN EFFICIENCY VS. MOBILITY RATIO FOR THE DIRECT LINE DRIVE.

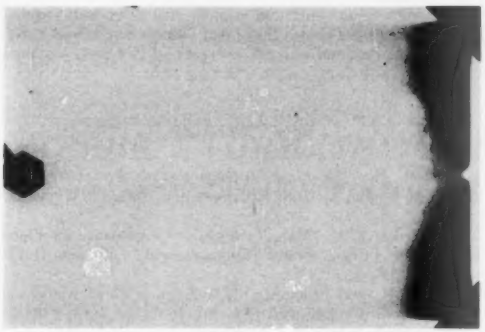

FIG. 7 — AREAL SWEEPOUT PATTERN AT INITIAL BREAKTHROUGH FOR THE STRAIGHT LINE DRIVE. MOBILITY RATIO = 8.3.

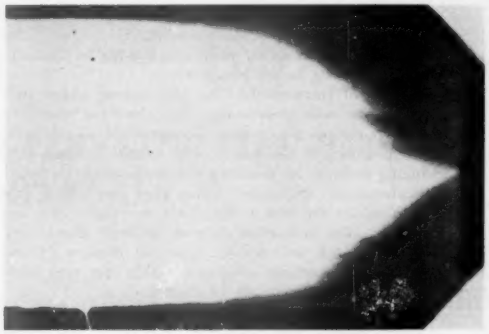

FIG. 8 — AREAL SWEEPOUT PATTERN AT INITIAL BREAKTHROUGH FOR THE STRAIGHT LINE DRIVE. MOBILITY RATIO = 1.0.

It may be noted by comparing Fig. 6 with Fig. 4 that the areal sweepout efficiency for the line drive pattern is less responsive to changes in mobility ratio than is that for the five-spot pattern.

Also shown in Fig. 6 are the sweepout pattern efficiencies obtained by a modified potentiometric model technique.[2] The discrepancies between these two sets of data are believed to be greater than the possible experimental error in the *X*-ray technique, and may be due, at least in part, to the stepwise procedures employed in the modified potentiometric model technique.

## PROBABLE RELIABILITY OF AREAL SWEEPOUT EFFICIENCIES OBTAINED BY THE X-RAY TECHNIQUE

In the study of frontal advance patterns with the *X*-ray technique, the small permeability variations which are usually found in both natural and synthetic porous media causes some sections of the front to advance disproportionately, the net result being the formation of fingers of the invading fluid toward the output well. As might be expected, this phenomenon is more pronounced at low mobility ratios and becomes practically non-existent at mobility ratios above one. Figs. 7, 8 and 9 show the initial breakthrough pattern on a straight line drive section for mobility ratios of 8.3, 1.0, and 0.48 respectively. By comparing these three figures it may be seen that: (1) at the higher mobility ratio (Fig. 7), there is no apparent distortion of the front that could be caused by fingers; (2) at a mobility ratio of one (Fig. 8) there are small fingers which do not influence the pattern unduly; (3) at a mobility ratio of 0.48 (Fig. 9) the fingering is of such an extent that the areal sweepout efficiency measured at this initial breakthrough may be appreciably lower than would be obtained if the frontal advance were uniform.

It would thus appear that the values of areal sweepout efficiency shown in Figs. 4 and 6 are substantially correct for mobility ratios above one, but that the use of the initial breakthrough of the invading phase as the criterion for determining areal sweepout efficiencies may result in erroneous values for the lower mobility ratios. Errors thus incurred would cause the measured areal sweepout efficiencies to be low and the percentage error would increase (as the amount of fingering increases) with decreasing mobility ratios.

## FURTHER APPLICATIONS OF THE RADIOGRAPHIC TECHNIQUE TO FLUID FLOW STUDIES

By the use of specially constructed porous plates, factors which affect areal sweepout patterns other than mobility ratio may be studied such as:

1. The effect of barriers (either natural or artificially formed in the reservoir) upon the area swept at breakthrough.

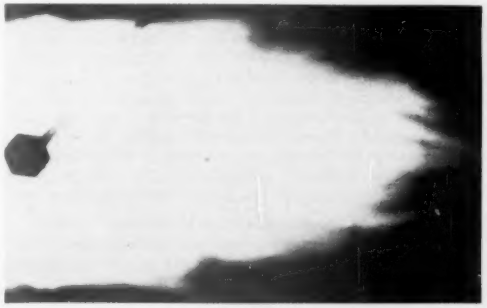

FIG. 9 — AREAL SWEEPOUT PATTERN AT INITIAL BREAKTHROUGH FOR THE STRAIGHT LINE DRIVE. MOBILITY RATIO = 0.48.

2. The effect of horizontal strata of different permeabilities covering all or a part of the reservoir.
3. The effect of permeability variations leading to channeling or by-passing in the reservoir.
4. The effect of fractures and fracture system either surrounding the wells or extending throughout the reservoir.
5. The effect of free gas in the reservoir when an oil bank build-up ahead of the water flood creates a constantly changing mobility ratio during the progress of the flood.

The displacement efficiencies within the area swept can also be studied by the use of the *X*-ray technique and the method of obtaining saturation data as outlined above. The effect of factors such as viscosity, rate and relative permeability on the displacement efficiency within the area contacted by the flooding fluid may be studied.

## CONCLUSIONS

1. A technique using the principles of radiography has been developed which may be used to study the effect of factors which influence the areal sweep efficiency in secondary recovery practices.
2. The extension of this technique to include the determination of the fluid saturation by means of the optical density of the radiographic plate makes possible quantitative studies of displacement efficiencies within the area swept.
3. Studies on five-spot and straight line drive well spacing patterns have shown that areal sweepout efficiencies may vary by as much as 50 per cent of the reservoir area between mobility ratios of 0.1 to 10.0.

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# BUBBLE FORMATION IN SUPERSATURATED HYDROCARBON MIXTURES

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## ABSTRACT

In many investigations of the performance of petroleum reservoirs the assumption is made that the liquid, if below its bubble-point pressure, is at all times in equilibrium with gas. On the other hand, observations by numerous investigators have indicated that gas-liquid systems including hydrocarbon systems, may exhibit supersaturation to the extent of many hundred psi in the laboratory. Up to the present, there has been no reliable data on which to judge the actual extent of supersaturation under conditions approaching those existing in petroleum reservoirs.

The work reported here deals with observations and measurements on mixtures of methane and kerosene in the presence of silica and calcite crystals. Bubbles were observed to form on crystal-hydrocarbon surfaces in preference to the glass-hydrocarbon interface or to the body of the liquid. Statistically, it was found that the number of bubbles formed per second per square centimeter of crystal surface was a function of the supersaturation only, and the function was evaluated graphically.

Supersaturations were observed up to 770 psi, under which condition bubbles formed quickly and with considerable violence. With decreasing degrees of supersaturation, the frequency of bubble formation became less, until at 30 psi supersaturation and lower, no bubbles were observed to form, even though the observation at 30 psi was continued for 138 hours. It was found that silica and calcite crystals had identical effects, within experimental error, in accelerating the formation of bubbles, and that small amounts of water and crude oil had no effect on the results.

It is shown that the maximum supersaturation that can exist in a reservoir may be calculated from the data presented and from the area of the rock surface. It is also shown that the number of bubbles formed in the reservoir, in order of magnitude, may be calculated for any rate of pressure decline imposed on the reservoir by production. The bearing of the number and distribution of bubbles on reservoir performance is discussed.

## INTRODUCTION

A liquid system is supersaturated with gas when the amount of gas dissolved exceeds that corresponding to equilibrium at the existing pressure and temperature. The degree of supersaturation may be conveniently expressed as the difference between the bubble-point of the mixture and the prevailing pressure. Thus, if a mixture having a bubble-point of 1,000 psi at a given temperature exists in single liquid phase at 700 psi at the same temperature, it is supersaturated to the extent of 300 psi.

There are many examples of high supersaturations, mostly in aqueous solutions, reported in the literature. Thus, Kenrick, Wismer and Wyatt[1] showed that water may be saturated with oxygen, nitrogen or carbon dioxide at 100 atmospheres, and the pressure reduced to one atmosphere without producing bubbles immediately. When liquids are in a state of tension, they may be considered as supersaturated at least to the extent of the tension. The tensile strength of water has been reported as 30 atmospheres by Meyer,[2] 60 atmospheres by Budgett,[3] 30 to 50 atmospheres by Temperley and Chambers,[4,5] 200 atmospheres by Dixon,[6] and 223 atmospheres by Briggs.[7]

Vincent[8,9] determined the tensile strength of a mineral oil as 45 psi. Gardescu[10] maintained pressures for short times in a model reservoir at 115 psi below the bubble-point.

It should be noted that the high supersaturations observed were obtained on systems carefully purified to remove particles or surfaces which might promote the formation of bubbles. These "nuclei" were considered as contaminants which interfered with the determination of a property of the liquid. In

[1]References given at end of paper.

Manuscript received in the Petroleum Branch office June 10, 1952. Paper presented at the Petroleum Branch Fall Meeting in Houston, Tex., Oct. 1-3, 1952.

petroleum reservoirs, the mineral and water surfaces with which oil is in contact must be accepted as essential parts of the system under investigation. Further, the data, to be of greatest utility for engineering purposes, should deal quantitatively with the number of bubbles formed in the reservoir under prevailing conditions. It is clear that observations of the maximum supersaturations that can be maintained for unspecified short periods, cannot yield this type of information.

In the direction of developing a quantitative approach to the phenomenon of supersaturation, it was noted that bubbles are always formed on a solid surface rather than in the liquid phase. Their formation appears to be distributed at random both as regards time and location on the solid surface. It would therefore be expected that a sufficiently large number of observations would give, at a fixed supersaturation, a constant average number of bubbles formed per square centimeter of surface per second. This theory of random formation of bubbles is in accord with the wide variation of supersaturations reported in the literature on apparently identical systems, and is supported by the data obtained in this investigation.

## EXPERIMENTAL METHOD

Methane used in this investigation was the commercial material, obtained in 1,500 psi cylinders and rated as 96 per cent pure, the impurities being ethane, propane, nitrogen and oxygen. The kerosene had an API gravity of 46.3°, with an average boiling point (10 per cent intervals) of 344°F. The quartz and calcite minerals used were accurately cut from large natural crystals. The crude oil used was from the East Texas Field.

The choice of test methods was complicated by the fact that at high supersaturations, glass was the only solid found which did not accelerate bubble formation. In a steel observation cell, bubbles were observed to form repeatedly at certain points on the steel surface and on the exposed surfaces of the gaskets. The slightest scum on a mercury surface would promote bubble formation at high supersaturations, although no trouble from this source was observed in the lower range of values. However, at low supersaturations, due to the longer periods of observation required, the greater effect of diffusion of gas across gas-liquid boundaries eliminated the possibility of employing such surfaces.

Two methods were therefore employed. In the first method, used at high supersaturations, the system was confined in a glass tube with a gas-liquid contact as an upper boundary. For lower supersaturations, the system was confined above carefully purified mercury. As will be shown later, diffusion was not a factor for the periods of observation required in the first method, while no bubbles were observed to form on the mercury surface in the low supersaturation tests for which the second method was used.

In both methods, filtered kerosene and methane were agitated together in an Aminco mixing bomb for several hours, at 500 psi or 1,000 psi and room temperature. An amount of gas was released that would cause a slight drop in pressure, and shaking continued. A rise in pressure to the original value indicated that saturation was complete. The gas phase was bled off from the mixture at constant pressure, and the pressure then raised to 2,000 psi, to give an unsaturated solution of accurately known bubble-point.

In the first test method, used for high supersaturation values, quartz or calcite crystals were stacked in a test tube within a Penberthy visual cell as shown in Fig. 1. The crystals had rectangular faces of accurately known areas, the total area for each crystal averaging about 4.5 sq cm. Sufficient kerosene containing no dissolved gas was introduced into the tube to cover the bottom and one-half of the sides of the lowest crystal. The pressure in the cell was then raised to the test pressure, usually 1,000 psi, by introducing methane, and enough saturated kerosene was added to raise the liquid level to the center of the next higher crystal, holding the pressure constant.

A valve, connecting the cell to a fixed and calibrated orifice, was then opened, and the pressure allowed to fall. An electric timer was started when the valve was opened, and the time at which the first bubble appeared was noted. In conjunction with the calibration curve, the time indicated the pressure, and thus the supersaturation pressure, at which the bubble formed. A typical calibration curve is shown in Fig. 2. Where warranted by temperature fluctuations, corrections based on several calibration curves made at different room temperatures, were applied.

The appearance of a bubble terminated a run, since considerable mixing and evolution of gas generally accompanied its formation. To prepare for the next run, the cell was then allowed to fall to atmospheric pressure to desaturate its contents. It was then again brought to the test pressure by the induction of gas, and live kerosene was added until the liquid level rose to the center of the next higher crystal. The pressure was allowed to fall by opening the valve to the calibrated orifice, and the observation repeated. After the glass tube containing the crystals was filled above the top crystal, the tube was emptied, and another set made. Normally, 85 observations constituted a series, which could be analyzed

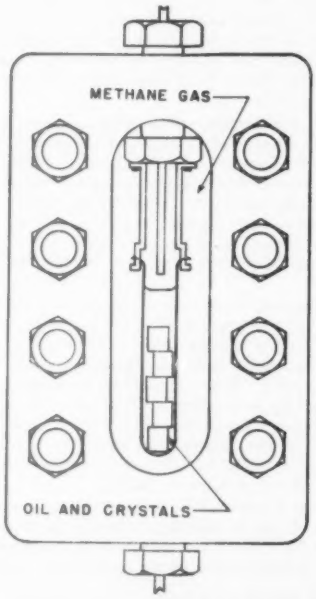


FIG. 1 — WINDOWED CELL FOR HIGH SUPERSATURATION TESTS.

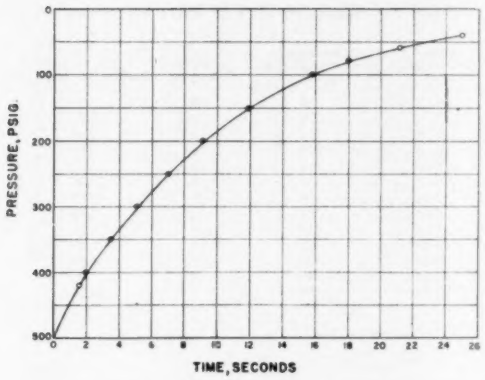


FIG. 2 — TYPICAL ORIFICE CALIBRATION CURVE.

statistically. On one series (Series E), in which the crystal area was twice the usual area, 170 observations were made to provide more points in the high supersaturation range.

The data desired from this method were (1) the number of bubbles formed in a definite narrow range of supersaturation values, (2) the total number of seconds during which the system was in this range, and (3) the area of crystal-oil interface involved. To obtain (1), the supersaturation ranges were selected to correspond to two-second intervals on the orifice calibration curve, and the number of bubbles observed in each of these intervals totaled. To obtain (2) for a given interval, two seconds for each test that went through the interval were added to the time spent in the interval by those tests terminating in the interval; (3) was determined as the average crystal-oil area for the tests terminating in the interval involved.

An example of the calculation of the number of bubbles formed per second per square centimeter (termed the frequency) by this method follows. In the interval zero to two seconds, corresponding to the supersaturation range of 0-95 psi supersaturation, no bubbles were formed and the frequency is zero. In the interval two to four seconds, corresponding to 95-165 psi supersaturation, nine bubbles were formed, and 76 tests passed through the interval without forming bubbles. The actual time spent in the interval in those tests terminated by bubble formation in the interval is shown in the first nine terms in the first bracket of the denominator below.

$$F = \frac{9}{[1.1+1.2+0.9+1.5+0.3+1.4+0.7+1.5+0.6+(76)\,2]\,[4.47]} = 0.0125$$

The term 4.47 represents an average of the crystal areas exposed to live oil. The frequency, thus determined, represents the probability that a bubble will form in one second on one square centimeter of crystal surface, at the average supersaturation in the interval.

In the second method, employed where the degree of supersaturation was so low that long times of standing were required, mixtures were confined above mercury as shown in Fig. 3. In order that no reaction products between kerosene and mercury could be formed and act as nuclei, the kerosene was distilled over sodium. After this precaution was taken no bubbles formed on the mercury surface.

In determining the frequency of bubble formation by this method the cell was assembled as shown in Fig. 3 with a single crystal inside the glass tube. The cell was then evacuated to less than 1 mm mercury pressure and purified mercury was drawn into the cell through the bottom connection until the inverted test tube was completely immersed in and filled with mercury. Water was then pumped into the top of the cell, with mercury being withdrawn from the bottom, until the test tube could be observed to a position well below the crystal, which had floated to the top of the test tube. The pressure in the cell was then adjusted to 1,000 psi which was 500 psi above the bubble-point of the mixture. A sample of kerosene-methane mixture was then introduced into the open lower end of the test tube, and then collected above the mercury.

Then the pressure on the system was lowered by bleeding off water from the top of the cell until the desired supersaturation was reached. The system was then allowed to stand until a bubble was observed to form, or in one case, until 138 hours had elapsed without bubble formation. After a bubble had been observed, the pressure was quickly raised to 1,700 psi, so as to redissolve the bubble before appreciable diffusion had taken place. One filling could thus be used for a number of tests without refilling the tube.

To correct for small variations of bubble-point with temperature, which could not be considered as negligible in this method, the magnitude of the bubble-point variation was

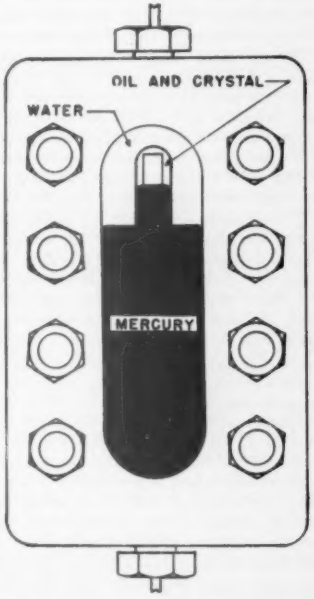


FIG. 3 — WINDOWED CELL FOR LOW SUPERSATURATION TESTS.

estimated by using available *K*-value charts for methane in a 200 molecular weight solvent. Correction was then applied by raising or lowering the pressure in the cell to keep the supersaturation of the liquid constant.

The frequency, as measured by this method, was simply the reciprocal the time which elapsed at a given supersaturation before a bubble was observed, divided by the crystal area.

## DISCUSSION OF RESULTS

At any vapor-liquid interface in a supersaturated system vaporization is taking place. In the first method employed, such an interface existed and it was necessary to determine what influence, if any, this process exerted on the measured frequencies. To this end, two series of tests, "A" and "B," were run, the first involving an initial rate of pressure decline of 55 psi per second, while the initial pressure decline rate for Series "B" was 30 psi per second. If the loss of gas at the interface were effective in lowering the supersaturation, it should be more pronounced in the second series, and the frequency of bubble formation should be lower. Reference to Tables I and II, and to Fig. 4, in which the average frequencies for all series are plotted against the supersaturation, shows no effect in this direction. All subsequent runs by Method 1 were made with pressure decline rates higher than those used in Series "B," so as to eliminate the possibility of this source of error.

Both Series "A" and "B" were made with kerosene saturated with methane at 500 psi in the presence of quartz crystals. The temperature of saturation and testing ranged from 84°F to 86°F. As in the other series investigated, the errors introduced by this variation did not exceed others inherent in the method and no correction for temperature was applied.

Series "C" was made with a mixture of kerosene and methane with a bubble-point of 1,000 psi, to determine the effect of absolute saturation pressure on bubble frequency. The data are contained in Table III and are plotted in Fig. 4. It is seen that, within the error involved in statistical observations of this type, there is no difference between liquids of different bubble-point at the same supersaturation. The crystals used in this series were quartz, as in the two previous series.

Series "D" was made with 1,000 psi bubble-point oil, and in all respects was similar to Series "C" except that calcite crystals were substituted for quartz. The data are shown in Table IV and are plotted on Fig. 4. It is seen that the composite curve drawn fits the data of this series as well as the previous data, and that calcite must be considered as equivalent to quartz as an accelerator of bubble formation.

In Series "E," a volume of saturated oil sufficient to cover twice the area of crystal as in previous tests was introduced. In other respects the runs were identical with those of Series "D." An examination of Table V, and the points for this series plotted on Fig. 4, indicates that the frequency of bubble formation, in terms of bubbles formed per second per square centimeter of crystal surface, is comparable to that obtained in the other runs. In order that sufficient data for statistical purposes should be available, twice as many runs as usual were made under the conditions of this series.

Undiluted crude oil could not be used in the tests described, because its dark color interfered with the observation of bubbles. However, it was thought possible that nuclei might be present in crude oil and might influence the frequency data obtained. In Series "F," therefore, the maximum amount of East Texas crude oil which would still allow visibility, 1.6 per cent, was added to the system. Other conditions were the same as in Series "E," *i.e.*, 1,000 psi bubble-point oil in contact with calcite. As shown in Table VI and Fig. 4, there is no discernible effect of the addition of crude oil to the system.

Data on frequencies at supersaturations below 50 psi, where effects of diffusion at the gas-liquid interface were considered to render results by the first method of investigating unreliable, are shown in Table VII. The frequencies are also

**Table I — Summary of Test Data for Series "A"**

| Time Interval Sec. | Average Supersaturation psi | No. Bubbles Observed | Bubble Frequency Bubbles/cm²/sec x 100 |
|---|---|---|---|
| 0- 2 | 48 | 0 | 0 |
| 2- 4 | 130 | 9 | 1.25 |
| 4- 6 | 194 | 13 | 2.08 |
| 6- 8 | 249 | 16 | 3.34 |
| 8-10 | 295 | 14 | 3.50 |
| 10-12 | 333 | 9 | 3.44 |
| 12-14 | 364 | 7 | 3.79 |
| 14-16 | 391 | 6 | 4.96 |
| 16-18 | 412 | 4 | 5.14 |
| 18-20 | 427 | 3 | 6.04 |
| 20-22 | 439 | 2 | 6.21 |
| 22-24 | 449 | 0 | 0 |
| 24-26 | 458 | 1 | 10.15 |

**Table II — Summary of Test Data for Series "B"**

| Time Interval Sec. | Average Supersaturation psi | No. Bubbles Observed | Bubble Frequency Bubbles/cm²/sec x 100 |
|---|---|---|---|
| 0- 2 | 32 | 0 | 0 |
| 2- 4 | 86 | 0 | 0 |
| 4- 6 | 129 | 7 | .962 |
| 6- 8 | 166 | 10 | 1.52 |
| 8-10 | 197 | 9 | 1.55 |
| 10-12 | 227 | 11 | 2.26 |
| 12-14 | 254 | 11 | 2.86 |
| 14-16 | 278 | 8 | 2.68 |
| 16-18 | 301 | 8 | 3.52 |
| 18-20 | 321 | 7 | 4.30 |
| 20-22 | 338 | 5 | 4.76 |
| 22-24 | 354 | 3 | 5.20 |
| 24-26 | 369 | 3 | 7.89 |
| 26-28 | 382 | 1 | 3.99 |
| 28-30 | 394 | 1 | 6.38 |
| 30-32 | 405 | 1 | 44.7 |

**Table III — Summary of Test Data for Series "C"**

| Time Interval Sec. | Average Supersaturation psi | No. Bubbles Observed | Bubble Frequency Bubbles/cm²/sec x 100 |
|---|---|---|---|
| 0- 2 | 80 | 0 | 0 |
| 2- 4 | 216 | 10 | 1.39 |
| 4- 6 | 318 | 21 | 3.68 |
| 6- 8 | 406 | 22 | 5.22 |
| 8-10 | 484 | 15 | 7.26 |
| 10-12 | 550 | 9 | 7.51 |
| 12-14 | 609 | 5 | 12.85 |
| 14-16 | 663 | 2 | 15.96 |
| 16-18 | 709 | 0 | 0 |
| 18-20 | 747 | 1 | 18.61 |

**Table IV — Summary of Test Data for Series "D"**

| Time Interval Sec. | Average Supersaturation psi | No. Bubbles Observed | Bubble Frequency Bubbles/cm²/sec x 100 |
|---|---|---|---|
| 0- 2 | 80 | 0 | 0 |
| 2- 4 | 216 | 14 | 2.01 |
| 4- 6 | 318 | 17 | 3.08 |
| 6- 8 | 406 | 18 | 4.71 |
| 8-10 | 484 | 16 | 6.63 |
| 10-12 | 550 | 12 | 9.95 |
| 12-14 | 609 | 5 | 10.25 |
| 14-16 | 663 | 2 | 12.09 |
| 16-18 | 709 | 0 | 0 |
| 18-20 | 747 | 0 | 0 |
| 20-22 | 778 | 1 | 76.5 |

**Table V — Summary of Test Data for Series "E"**

| Time Interval Sec. | Average Supersaturation psi | No. Bubbles Observed | Bubble Frequency Bubbles/cm²/sec x 100 |
|---|---|---|---|
| 0- 2 | 81 | 0 | 0 |
| 2- 4 | 220 | 43 | 1.69 |
| 4- 6 | 322 | 51 | 2.98 |
| 6- 8 | 406 | 42 | 4.68 |
| 8-10 | 481 | 21 | 6.15 |
| 10-12 | 548 | 8 | 7.68 |
| 12-14 | 605 | 4 | 11.13 |
| 14-16 | 656 | 1 | 16.46 |

**Table VI — Summary of Test Data for Series "F"**

| Time Interval Sec. | Average Supersaturation psi | No. Bubbles Observed | Bubble Frequency Bubbles/cm²/sec x 100 |
|---|---|---|---|
| 0- 2 | 81 | 0 | 0 |
| 2- 4 | 220 | 12 | 1.71 |
| 4- 6 | 322 | 18 | 3.13 |
| 6- 8 | 406 | 20 | 4.98 |
| 8-10 | 481 | 17 | 7.71 |
| 10-12 | 548 | 9 | 8.49 |
| 12-14 | 605 | 4 | 7.85 |
| 14-16 | 656 | 4 | 14.2 |
| 16-18 | 700 | 1 | 17.2 |

**Table VII — Summary of Low Supersaturation Tests by Second Method**

| Super-saturation psi | Dry Quartz Crystal | | | Water-Wet Crystal | | |
|---|---|---|---|---|---|---|
| | No. Bubbles Observed | Time Before First Bubble, Sec. Range | Average | No. Bubbles Observed | Time Before First Bubble, Sec. Range | Average |
| 50 | 10 | 36.3-87.2 | 56.7 | 10 | 39.1-77.2 | 58.1 |
| 40 | 4 | 104-600 | 287.4 | 6 | 102-343 | 236.5 |
| 30 | None in 138 hours | | | None in 27 hours | | |

plotted on Fig. 4. As indicated in the table, 14 observations on dry quartz crystals were made and 16 on quartz crystals which had been wet with water. It is seen that the presence of water has no discernible effect. It should also be noted that the data obtained by this method fit very well on the composite curve obtained by the method employed for investigation systems of high supersaturation. The conformity of the data by the two methods in the region of low supersaturation is further evidence that the error due to diffusion in the first method is not appreciable under the conditions employed.

The composite curve shown in Fig. 4 was drawn as the best curve to fit all of the data obtained. It is of interest to note, however, that this curve fits the points for each series almost as well as any that could be drawn.

## SIGNIFICANCE OF DATA IN PETROLEUM RESERVOIR STUDIES

In the work described, an effort was made to duplicate the essential conditions which affect the formation of bubbles in petroleum reservoirs, insofar as these conditions are known. It is appropriate, therefore, to discuss some of the implications of the results in regard to a reservoir to which they may apply.

When oil is produced from a reservoir, the pressure normally declines, even if an effective water-drive is present. Some reservoirs, such as the East Texas reservoir, are so undersaturated, that substantially their entire recoverable contents may be produced at restricted rates without the pressure falling below the bubble-point of the oil. More commonly, however, the oil becomes supersaturated in the early stages of production, even though it may have been highly undersaturated initially.

On the basis of data presented here, bubbles would be expected to form only after the supersaturation exceeds 30 psi. Supersaturation in excess of this figure and bubbles will naturally occur first in the low-pressure regions in the immediate vicinity of the producing wells. Because of the comparatively high velocities and intimate contact between gas and oil, substantial equilibrium should exist between the two phases at this location under normal flowing conditions.

As the reservoir pressure declines, and the isobar corresponding to 30 psi supersaturation moves outward from the wells, bubble formation will follow it. If the reservoir oil is uniform in composition and subject to normal gravitational pressure distribution, the surfaces connecting the bubbles farthest from the wells will be an inverted and truncated cone, with sides of constant slope. The expanding cone will follow the isobar to the limit of the reservoir or to the region of interference with another well.

When a bubble is formed, diffusion of gas from the surrounding oil begins, decreasing the supersaturation in its immediate vicinity and expanding the bubble. Surface forces, tending to compress the bubble, become negligible when its radius exceeds about .01 mm. (If the surface tension is taken as five dynes per centimeter, and bubble radius, or the radius of the pore through which the bubbles are expanding, is .01 mm the excess pressure in the bubble is only .15 psi.) Due to the phenomenon of supersaturation, the equilibrium pressure of the gas dissolved in the oil is at least 30 psi higher than the pressure inside the bubble initially, and rapid evolution of gas occurs. This situation accounts for the observation that bubbles expand to about 1 mm in radius almost instantly after they are formed on crystal surfaces.

Aspects of reservoir behavior on which the data presented may shed some light may be listed as follows:

1. The extent to which reservoir fluids may be considered to be truly at equilibrium. This is a function of the number of bubbles formed and the rate of diffusion from the oil into the gas phase as well as the rate of pressure decline imposed by production from the reservoir.

2. The order of magnitude of the number, size and distribution of bubbles formed in reservoirs.

As a first step in estimating the departure from equilibrium, the maximum supersaturation possible in the reservoir may

be estimated. It is evident that this maximum will occur in the early life of the reservoir as bubbles are forming, rather than at a later date when concentration gradients have been lowered by diffusion. As an example, consider a reservoir rock with a surface area of 450 sq cm per cu cm. (The unit area assumed corresponds to a rock made up of spheres .01 cm in diameter with rhombohedral packing.) From the slope of the frequency curve, Fig. 4, we may estimate the bubble frequency, as the curve approaches its intercept, as $10^{-4}$ bubbles per second per square centimeter per psi supersaturation. Thus, if a supersaturation of only 31 psi could persist for one day, more than four thousand bubbles would be formed in each cubic centimeter of rock. The aggregate volume of gas, if each bubble were the equivalent of one mm in diameter, would be more than twice the entire rock volume. It is clear, therefore, that the maximum supersaturation is less than one psi in excess of the intercept value on Fig. 4, and differs from this value by less than the uncertainty in our measurement of the intercept. The intercept value of 30 psi will therefore be taken as the maximum value of supersatuartion that can exist more than momentarily in a reservoir.

It should be noted that while 30 psi represents the maximum supersaturation in a reservoir, the reservoir as a whole will never have an average supersaturation approaching this figure. While bubbles are forming in one position, oil in contact with bubbles already formed in another position will be substantially at equilibrium with them. If the reservoir pressure remains constant for a time, the oil and gas phases will approach complete equilibrium due to diffusion. If the pressure is declining at a uniform rate, supersaturation in excess of 30 psi and bubble formation will occur only if the diffusion rate into bubbles already formed is insufficient to prevent such supersaturations at all points. We thus have a criterion and a means of determining the number of bubbles that is necessary and sufficient to provide the amount of diffusion required for a given rate of pressure decline. This requirement may be expressed

$$\frac{dp}{dt} = \frac{dp_s}{dt} = \frac{Q}{V_o} \cdot \frac{dp_s}{ds} \quad \ldots\ldots\ldots (1)$$

where $\frac{dp}{dt}$ is the rate of pressure decline imposed by production from the reservoir;

$\frac{dp_s}{dt}$ is the rate of decline of saturation pressure due to

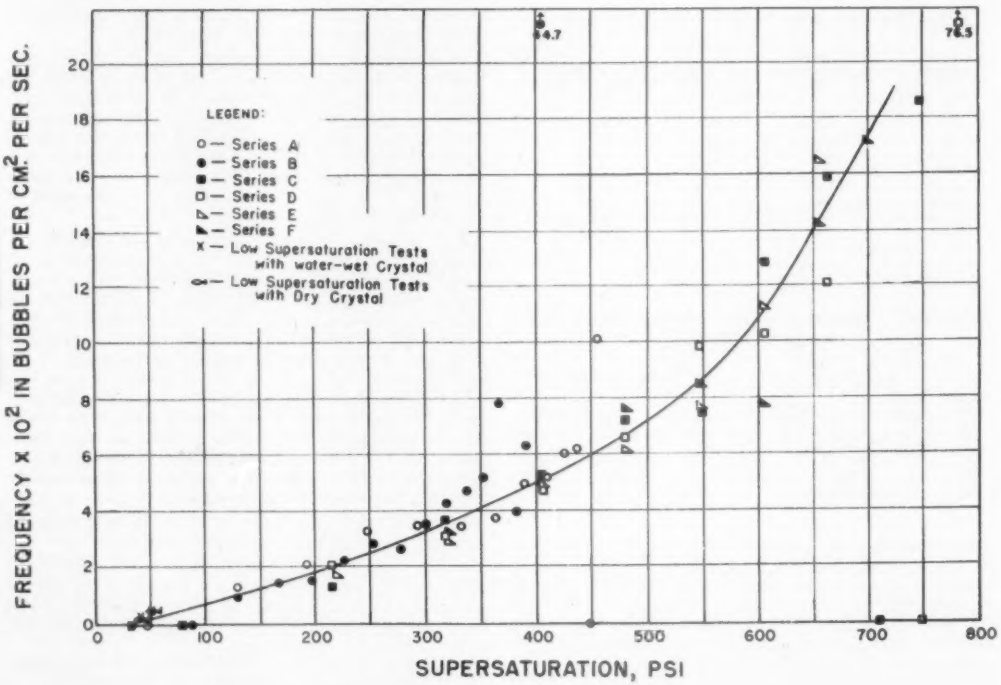


FIG. 4 — COMPOSITE BUBBLE FREQUENCY CURVE.

diffusion at the point in the region of influence of a bubble farthest removed from the bubble;

$Q$ is the volume of gas, in surface measure, which diffuses through the volume $V_o$ of oil in unit time;

$\frac{dp_e}{ds}$ is the decrease in equilibrium pressure due to the evolution of unit volume, in surface measure, of dissolved gas.

In determining the number of bubbles required to reduce the maximum saturation pressure at a rate equal to the reservoir pressure decline, steady state spherical flow is assumed. As shown by Bertram and Lacey,[21] the entire effect of the reservoir rock on diffusion may be expressed as a factor of about 0.8, representing the increased length of path attributable to the presence of the aggregate. (The truth of this statement is evident when it is remembered that both the amount of diffusible gas and the cross section available for diffusion are decreased by a factor representing the fractional porosity. Except for the above correction, therefore, the presence of the reservoir rock will be ignored.)

We may write, for each bubble in the reservoir,

$$Q = 0.8\frac{4\pi D(S_e - S_b)}{\frac{1}{r_b} - \frac{1}{r_e}} \quad \ldots\ldots\ldots \quad (2)$$

where $D$ is the diffusion constant, and $r_b$ and $r_e$ are respectively the radius of the bubble and of the region of influence of the bubble, and $S_b$ and $S_e$ are the concentrations of gas at $r_b$ and $r_e$, respectively. Each cubic foot of the reservoir may be assumed to contain $N$ bubbles, each of which has a region of influence comprising $\frac{1}{N}$ cu ft. $r_e$ may be expressed in terms of $N$ as

$$r_e = \sqrt[3]{\frac{3}{4\pi N}} \quad \ldots\ldots\ldots \quad (3)$$

$V_o$ in equation (1) is simply $\frac{1}{N} = \frac{4}{3}\pi r_e^3$.

Equations (1), (2) and (3) may then be combined to give

$$\frac{dp}{dt} = \frac{dp_e}{dt} = \frac{3.2\pi ND(S_e - S_b)}{\frac{1}{r_b} - \sqrt[3]{\frac{4\pi N}{3}}} \frac{dp_e}{ds} \quad \ldots \quad (4)$$

If the relation between the saturation pressure, $p_e$, and the gas dissolved at this pressure $S_e$ be linear, then $\frac{S}{p_e} = K_e$, and

$$S_e - S_b = K_e(p_{e_e} - p_{e_b})$$

where $K_e$ is the slope of the pressure-solubility curve, and $p_{e_e}$ and $p_{e_b}$ are respectively, the equilibrium pressures at $r_e$ and $r_b$. Further, $\frac{dp_e}{ds}$, for a linear solubility relation, may be represented by $\frac{1}{K_e}$. For a reservoir in which the maximum supersaturation is 30 psi, the maximum value of $K_e(p_{e_e} - p_{e_b})$ must equal 30 $K_e$. As a final equation, relating the number of bubbles with the rate of pressure decline, we may write

$$\frac{dp}{dt} = \frac{dp_e}{dt} = \frac{96\pi ND}{\frac{1}{r_b} - \sqrt[3]{\frac{4\pi N}{3}}} = \frac{301\ ND}{\frac{1}{r_b} - \sqrt[3]{4.2N}} \quad \ldots \quad (5)$$

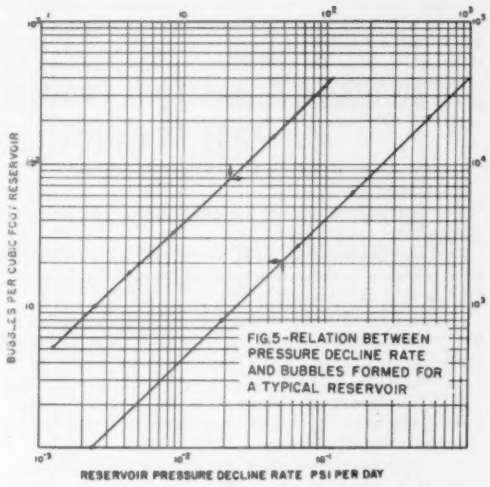
BUBBLES PER CUBIC FOOT RESERVOIR
RESERVOIR PRESSURE DECLINE RATE PSI PER DAY
FIG.5-RELATION BETWEEN PRESSURE DECLINE RATE AND BUBBLES FORMED FOR A TYPICAL RESERVOIR

FIG. 5 — RELATION BETWEEN PRESSURE DECLINE RATE AND BUBBLES FORMED FOR A TYPICAL RESERVOIR.

If, in accordance with our observation that bubbles almost instantly reach the radius of 1 mm we assign this value to $r_b$, and let $D$ equal $10^{-4}$ sq ft per hour as an average value,[22] we may calculate the number $N$ for a typical reservoir, for any value of $\frac{dp}{dt}$. Fig. 5 shows a plot of $N$ against the right-hand term of Equation (5). For reservoir pressure declines of 0.1, 1 and 10 psi per day, we may read corresponding numbers of bubbles per cu ft of reservoir satisfying the imposed conditions 40, 400 and 4,000. Due to the assumptions made in determining the diffusion rate, particularly the assumption of the value of $r_b$, the calculation must be considered correct only as to order of magnitude.

For a rock consisting of grains averaging 0.1 mm in diameter, there are about $10^6$ pores per centimeter cube, or some $3 \cdot 10^{10}$ pores per cu ft. It is clear that even at the most rapid reservoir pressure decline rates, only about one pore in a million will have a bubble originating in it. Where unaffected by flow, the gas will be present as a continuous enlarged bubble, encompassing many pores, surrounded by oil which is free of gas. When gradients are applied, the gas inside the continuous bubble will flow with a relative permeability characteristic of a much higher gas saturation than corresponds to the overall reservoir content, while the oil will be characterized by a relative permeability equal to the homogeneous fluid permeability of the rock. Equilibrium gas saturations,

at which gas exhibits zero relative permeability, should not exist in a reservoir with gas distributed in this manner. It is noteworthy that such behavior, although detectable by a decline in gas/oil ratio in the early life of gas-drive reservoirs and generally reported in laboratory studies, has been reported absent in all field measurements.[12]

## CONCLUSIONS

The data and calculations presented support the following conclusions:

1. Supersaturations as high as 770 psi are possible for short periods in a system consisting of kerosene, methane and crystals such as silica and calcite.

2. When crystals such as silica or calcite are present, bubbles invariably form on their surfaces rather than in the oil itself.

3. The tendency of bubbles to form in systems of this kind may be measured by the frequency, *i.e.*, the number of bubbles formed per second per square centimeter of crystal surface in contact with liquid.

4. Under the conditions of the tests, the frequency varied from .22 at 800 psi to zero at 30 psi saturation. No bubbles were observed to form at 30 psi supersaturation or lower, even though the test at 30 psi supersaturation was continued for 138 hours.

5. Calcite and silica surfaces are equally effective in promoting bubble formation.

6. The presence of water or crude oil, when added to the above system, had no measurable effect on bubble frequency.

7. From the bubble frequency measured, it may be calculated that maximum supersaturations in reservoirs cannot exceed 30 psi by more than a fraction of one psi, and that average supersaturations will be substantially less than this amount.

8. It is shown that the number of bubbles formed per cu ft of reservoir depends on the rate of diffusion of gas through oil and on the pressure decline rate imposed by production. For decline rates of 0.1, 1 and 10 psi per day, the number of bubbles formed will be 40, 400 and 4,000 per cu ft respectively, in order of magnitude.

9. Even at the higher rates of pressure decline, only one bubble is formed per million pores in the rock, suggesting that the increase of gas saturation in reservoirs takes place by the enlargement of gas bubbles into gas masses encompassing many rock pores.

10. Variations in the manner in which gas is distributed in permeable media may account for different relative permeabilities for the same gas saturation, and may explain discrepancies between laboratory and field data on the same type of rock.

## ACKNOWLEDGMENT

It is a pleasure to acknowledge the financial support of the Tennessee Gas Transmission Co., under whose fellowship this work was done, and the encouragement given by Herman A. Otto and O. H. Moore of this company. The interest taken in this project and the advice freely given by Harold Vance, head of the petroleum engineering department, A. and M. College of Texas, is also gratefully acknowledged.

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# PHASE AND VOLUMETRIC BEHAVIOR OF NATURAL GASES AT LOW TEMPERATURES

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## ABSTRACT

An experimental method and apparatus for the study of the low-temperature phase and volumetric behavior of volatile mixtures are described. The phase diagrams, including the critical points, and the volumetric behavior of a natural gas and a mixture of the natural gas with methane at temperatures from −40°F to −200°F and pressures to 1,200 psi are given.

## INTRODUCTION

Knowledge of the phase and volumetric behavior of mixtures of the light hydrocarbons at low temperatures is becoming increasingly important as interest in low-temperature separation processes increases. Distillation at low-temperatures has been used for some time to recover ethane and ethylene from natural gas and refinery gas for petrochemical uses. Removal of excess nitrogen from natural gas by distillation has been proposed as a means of increasing the capacity of gas transmission lines and of improving the marketability of the gas.[1,20] Evaluation of the latter process has been hampered, however, by the scarcity of data from which the phase behavior of natural gases at low temperatures might be predicted. While existing correlations of vaporization equilibrium constants may be used to predict the behavior of such mixtures at lower pressures, high-pressure computations often require knowledge of the location of the critical point of the system involved. Although correlations have been developed[17,22] for the prediction of the critical temperature and pressure of certain types of hydrocarbon systems, they do not apply to very volatile systems such as nitrogen-bearing natural gases. This paper describes the initial stages of an investigation of the low-temperature behavior of a number of natural gases and other gases of commercial interest. The experimental method and apparatus are described, and the phase and volumetric behavior of a natural gas and a mixture of the natural gas with methane are presented.

## PREVIOUS WORK

The published low-temperature vapor-liquid equilibrium data for hydrocarbons and mixtures of hydrocarbons with nitrogen and helium are listed in Table I. Most of these data are for binary systems, and the data of Stutzman and Brown[24] at 100 psi are the only data on a natural gas. The data of Bloomer and Parent[3] on the methane-nitrogen system, which have been published since this study was completed, are a valuable addition to the knowledge in this field. Prior to the publication of these data the only published critical point data on systems having critical temperatures below the ice point were those of Ruhemann,[21] on the methane-

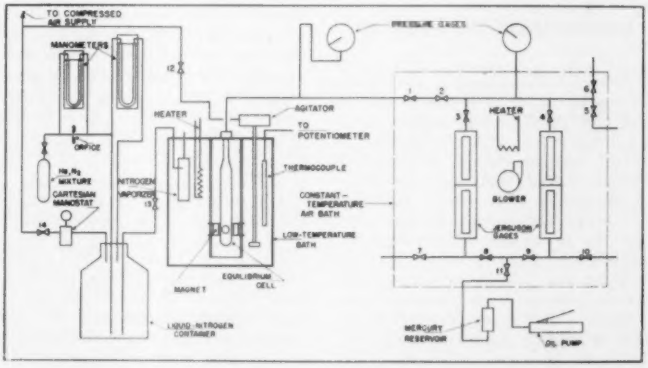


FIG. 1 — FLOW DIAGRAM OF APPARATUS

[1]References given at end of paper.

Manuscript received in the Petroleum Branch office April 29, 1952. Paper presented at the Petroleum Branch Fall Meeting in Houston, Tex., Oct. 1-3, 1952.

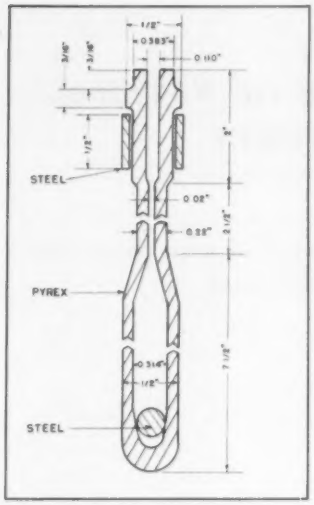


FIG. 2—CROSS-SECTION OF EQUILIBRIUM CELL

ethane system, and those of Eilerts, *et al*,[7] on a gas-condensate system. These data alone were not sufficient to allow accurate estimation of the critical behavior of the very volatile systems of engineering interest. While the publication of complete data on the methane-nitrogen system has done much to ease this problem, it is felt that additional data on more complex mixtures are still of considerable value.

## EXPERIMENTAL METHOD

The experimental method selected for this study is a modification of the dew-point bubble-point method used previously[10,11,7] at higher temperatures. In the usual application, a sample of the gas mixture, of known composition, is placed in a glass vessel maintained at constant temperature, and the pressure on the system is increased by introducing mercury, or an alloy of mercury and gallium, into the vessel. As the pressure is thus increased the mixture is caused to pass through its dew and bubble points, and these limits of the two-phase region are determined by visual observation. The freezing point of the mercury-gallium alloy limits this method of pressure variation to temperatures above −70°F. In the method described here, the pressure variation is accomplished by increasing the mass of sample contained in a cell of constant volume.

The dew-point bubble-point data resulting from this method can be analyzed to yield the equilibrium constants of the components of the mixture only if the mixture is binary. The method was chosen for this study of more complex mixtures because it permits precise location of the critical point of the mixture, because it decreases the number of analyses required, and because it allows concurrent determination of the volumetric behavior of the system. The dew-point bubble-point data, while not reducible to equilibrium constants, are still of value, since they offer a means of checking equilibrium constants predicted by generalized correlations.

## APPARATUS

A flow diagram of the apparatus is shown in Fig. 1. The phase separation occurs in a glass cell of about 12 ml volume which is suspended in a bath of pentane contained in a glass Dewar flask. Unsilvered strips on opposite sides of the flask allow observation of the contents of the equilibrium cell. The pentane bath is cooled by a stream of liquid nitrogen delivered from a metal Dewar flask by controlled air pressure. The temperature of the bath is held constant by manually adjusting a Variac which controls the heat input into the bath from a resistance coil. The bath is agitated by an air-driven agitator, and circulation of the bath liquid is encouraged by a draft tube mounted coaxially with the agitator. Agitation of the contents of the cell, to insure equilibrium, is obtained by moving a steel ball inside the cell with a magnet. The fitting by which the glass equilibrium cell is joined to the steel tubing which connects it with the gas reservoir was developed during this study and has been described previously.[6]

A cross-section of the glass equilibrium cell used in the majority of this study is shown in Fig. 2. It was found that such cells, made from Pyrex high-pressure gauge-glass tubing, will withstand pressures up to 1,300 psi for at least 24 hours. Though one cell burst at 800 psi after being tested to 1,250 psi and used at pressures up to 1,000 psi for two months, another cell was used for four months at pressures to 1,300 psi without failure. Because of the possibility of rupture of the cell, the low-temperature bath is mounted behind a steel safety plate and is observed through a Plexiglas-covered slit.

The neck of the cell and the line which leads to the gas reservoir are made of small-diameter tubing in order to minimize the volume between the body of the cell and valve 1, which separates the cell from the reservoir. This volume was determined to be about 3.7 ml.

**Table I — Published Phase Data on Hydrocarbon-Nitrogen-Helium Systems at Low Temperatures**

| System | Temperature Range °R | Pressure Range psia | Ref. |
|---|---|---|---|
| $He$-$N_2$ | 140-196 | 16-4,340 | 10 |
| | 123-202 | 5-3,675 | 16 |
| | 126-198 | 59-221 | 9 |
| He-$CH_4$ | 162-191 | 2,350 | 7 |
| | 162-229 | 2,645-3,380 | 8 |
| $N_2$-$CH_4$ | 152-194 | 14.7 | 19 |
| | 162-239 | 14.7-147 | 25 |
| | 180-322 | 40-740 | 3 |
| $CH_4$-$C_2H_4$ | 229-456 | 9-640 | 26 |
| | 304-492 | 7-588 | 14 |
| | 304-492 | 74-735 | 11 |
| $CH_4$-$C_2H_6$ | 321-336 | 441-588 | 18 |
| $CH_4$-$C_2H_6$-$C_3H_8$ | 305-492 | 74-735 | 11 |
| $C_2H_6$-$C_3H_8$ | 438-582 | 25-794 | 1 |
| Natural Gas Gas-Condensate | 222-330 | 100 | 24 |

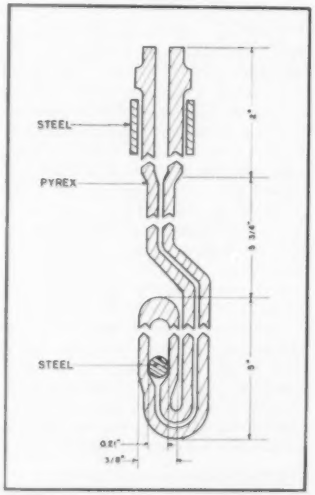


FIG. 3 — CROSS-SECTION OF INVERTED CELL

The gas reservoir consists of two liquid-level gauges, one of which is calibrated for internal volume and serves as a high-pressure gas burette; the other serves as a reservoir of high-pressure gas with which to fill the burette. Manifolds and valves connect these gauges to the rest of the apparatus, and an air bath maintains the reservoir at a constant known temperature. The pressure required to force the gas from the reservoir into the equilibrium cell is developed by a manually-operated hydraulic jack which displaces mercury into the liquid-level gauges.

The pressures in the equilibrium cell and gas reservoir are measured by Bourdon gauges having ranges of 0 to 2,000 psi and 0 to 5,000 psi, respectively. Comparison of these gauges with a dead-weight tester at intervals of several months indicates them to be accurate to ± 3 psi.

The temperature of the low-temperature bath is measured by a four-junction thermocouple, the EMF of which is measured with a Leeds and Northrup Type K-2 potentiometer. The thermocouple was calibrated against a platinum resistance thermometer; accuracy of the temperature measurement is judged to be ± 0.5°F or better.

## PROCEDURE

The gas reservoir is brought to a constant temperature of 100°F, and the gas burettes are evacuated and then flushed with the gas to be studied by alternately charging to a high pressure and venting to the atmosphere a number of times. The equilibrium cell is similarly purged at room temperature, and then suspended in the pentane bath. The bath is cooled to the desired temperature and then maintained at that temperature by throttling the flow of nitrogen through valve 13 and adjusting the Variac which controls the power to the heater element. The thermocouple and potentiometer will indicate temperature changes on the order of 0.01°F, and by constant attention, one person can control the temperature to 0.1°F, as long as no gross heat effects occur. The condensation of a large amount of gas causes temperature increases as large as 2°F, but the temperature is always stabilized to within 0.1°F of the control point before readings are made.

Increments of gas are added to the cell through valves 1 and 2, while maintaining a constant pressure in the reservoir by raising the mercury level.

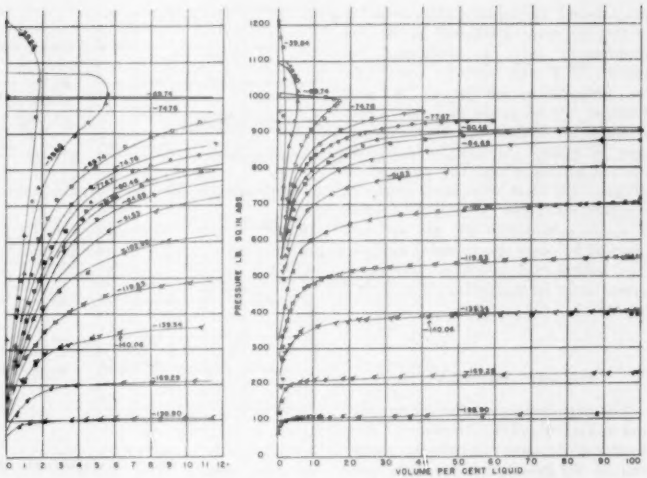


FIG. 4 — EXPERIMENTAL ISOTHERMS OF MIXTURE "A"

After each addition of gas the contents of the cell are agitated until the pressure no longer changes with time, and the cell is examined for the presence of liquid. The pressure at which dew is first apparent on the agitator ball is taken as the dew point; this pressure is usually considerably below that at which measurable liquid is formed. When liquid is present in the cell the mixture is agitated until neither pressure nor liquid level changes with time; the time required to reach this equilibrium varies from one minute at low pressures to ten minutes in the region of the critical point. The level of liquid in the cell is read against a platinum-inked scale fired to the cell; this scale is calibrated to read in volume per cent liquid.

Successive increments of the gas are added until the level of liquid reaches the constricted neck of the cell. Since the volume of the neck of the cell is only about 0.1 per cent that of the body of the cell, the mixture in the cell is considered to be completely liquefied, *i.e.*, at its bubble point, when the liquid enters the neck. Because this lack of an absolute boundary between the equilibrium cell and the rest of the apparatus might conceivably lead to error in the determination of the bubble point, the inverted cell shown in Fig. 3 was developed for more precise bubble point determinations. The results obtained with this cell agree with those obtained with the upright cell shown in Fig. 2, within the accuracy of the temperature and pressure measurements, so the latter cell was used throughout most of the investigation.

## RESULTS

The compositions of the two gases are given in Table II. The analysis of gas "A" was made by the Phillips Petroleum Co., which donated it, by low-

Table II — Properties of Gases Studied

| | Gas "A" | Gas "AB" |
|---|---|---|
| Composition, Mol % | | |
| Methane | 90.89 | 96.68 |
| Ethane | 4.40 | 1.60 |
| Propane | 1.91 | 0.70 |
| i-Butane | 0.33 | 0.14 |
| n-Butane | 0.60 | 0.20 |
| i-Pentane | 0.21 | 0.07 |
| n-Pentane | 0.13 | 0.05 |
| Hexanes | 0.15 | 0.05 |
| Heptanes-plus | 0.18 | 0.07 |
| Carbon Dioxide | 1.20 | 0.44 |
| Critical Pressure, psia | 925 | 765 |
| Critical Temperature, °F | –79 | –101 |
| Critical Density, g/ml | 0.230 | 0.183 |
| Molecular Weight | 18.40 | 16.90 |
| Pseudo Critical Press., psia | 676 | 674 |
| Pseudo Critical Temp., °F | –91 | –90 |

temperature fractionation. The behavior of this gas was established by the determination of 14 isotherms between –40°F and –200°F. Gas "AB" was prepared by mixing gas "A" with Phillips "Pure" grade methane, which is stated to contain less than one per cent of ethane, nitrogen, and carbon dioxide as impurities. The composition of gas "AB" was calculated from the composition of gas "A" and the amount of methane added to this gas, and was checked by mass spectrometer analysis. The behavior of gas "AB" was determined at seven temperatures from –80° to –200°F.

## PHASE BEHAVIOR

The experimental isotherms are plotted in Figs. 4 and 5. The shape of these isotherms is consistent with the composition of the gases; they are quite steep at low percentages of liquid, because of the presence of small amounts of heavy components, and much flatter at higher percentages of liquid, because of the absence of components more volatile than the major component, methane. Retrograde behavior is indicated by the higher temperature isotherms for each gas, which show double values of pressure at a single per cent of liquid.

The phase envelopes in Figs. 6 and 7 were obtained by crossplotting the data at constant percentages of liquid. The points shown in Figs. 6 and 7 are not experimental points, but are read from the curves, through the experimental points in Figs. 4 and 5.

The smoothness with which the data above about two per cent liquid crossplot, indicative of internal consistency, is regarded as favorable evidence of the reliability of the data. The steepness of the isotherms at low percentages of liquid makes accurate determination of the dew points very difficult, as is shown by the considerable scatter of the data around the dew point lines in Fig. 6 and 7, and these lines are therefore considered as approximations only. Bubble points read from the smoothed curves of Figs. 6 and 7 are tabulated in Table III.

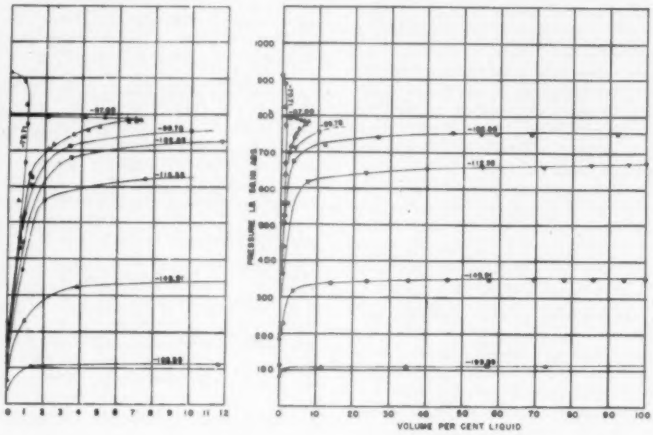


FIG. 5 — EXPERIMENTAL ISOTHERMS OF MIXTURE "AB"

From the phase diagrams the location of the critical point, the point to which all the constant-per-cent-liquid lines converge, can be definitely determined. The critical points given in Table II are believed to be accurate to ± 1°F and ± 10 psi.

Apart from the location of the critical point, the main utility of these phase data is their use to check vaporization equilibrium constants obtained from generalized correlations. Such a check is possible only along the boundary curves, where the composition of one of the phases is known. The inaccuracy of the dew point data given here makes such a check meaningful only along the bubble point line. In Table IV the experimental bubble point temperatures are compared with those calculated by use of the M. W. Kellogg equilibrium constants.[2,14] In these calculations carbon dioxide was assumed to behave as ethane, and it was necessary in some cases to make slight extrapolations of the correction factors involved in the Kellogg correlation. The calculations otherwise followed the procedure described in the references cited.

Since the product of the equilibrium constant and mol fraction of each of the components except methane is quite small, even at the higher temperatures, this comparison essentially reduces to a check of the methane constants. The agreement indicated in Table IV might be anticipated from the fact that the bubble point curve of each of the gases is not far removed from the vapor pressure curve of pure methane, since the equilibrium constants obtained from any correlation should be relatively more accurate in that region. However, it is significant that the agreement is good at the higher pressures, near the critical points of the mixtures, where the accuracy of most correlations, which do not include parameters allowing for the composition of the phases, decreases markedly. While this is not, of course, a severe test, it is felt that this agreement lends considerable support to the use of Kellogg constants for the prediction of the low-temperature behavior of methane in mixtures which, similar to these, are primarily methane.

**Table III — Smoothed Bubble Point Data**

| Temperature, °F | Bubble Point Pressure, psia | |
|---|---|---|
| | Gas "A" | Gas "AB" |
| –90 | 830 | |
| –100 | 735 | |
| –110 | 645 | 695 |
| –120 | 550 | 600 |
| –130 | 470 | 505 |
| –140 | 400 | 425 |
| –150 | 330 | 350 |
| –160 | 270 | 295 |
| –170 | 220 | 235 |
| –180 | 180 | 180 |
| –190 | 145 | 145 |
| –200 | 110 | 110 |

**Table IV — Comparison of Experimental and Calculated Bubble Points**

| Bubble Point Pressure, psia | Bubble Point Temperature, °F Gas "A" | | Gas "AB" | |
|---|---|---|---|---|
| | Experimental | Calculated | Experimental | Calculated |
| 150 | –188 | –184 | –189 | –187 |
| 200 | –175 | –172 | –178 | –174 |
| 300 | –155 | –154 | –158 | –157 |
| 400 | –140 | –140 | –144 | –143 |
| 500 | –128 | –127 | –131 | –131 |
| 600 | –115 | –115 | –120 | –118 |
| 700 | –104 | –105 | –109 | –109 |
| 800 | –93 | –95 | | |

## VOLUMETRIC BEHAVIOR

In order to calculate the density of the mixture in the equilibrium cell, the density of the gas at the conditions in the gas reservoir must be known so that the mass of gas delivered to the cell can be calculated from the measured volume delivered. In the absence of actual data on the gases studied, it was assumed that they were described by generalized compressibility-factor data for natural gases[2] which are said to be accurate to within about one per cent at the conditions of the reservoir.[4] With this assumption, the density of the total mixture in the cell can then be calculated, the volume of the cell being known. In this calculation due allowance was made for the volume between the body of the cell and the reservoir.

Check determinations of the density of propane, the actual density of which at both reservoir and cell conditions is known, indicated an error of only 0.2 per cent when the density of the fluid in the cell is as much as 0.5 grams/ml. Somewhat greater errors should be expected at lower densities because of the effect of the volume between the cell and reservoir. It is believed that the overall uncertainty in the volumetric data shown here, including that due to the use of the generalized data, is probably less than three per cent.

The volumetric behavior of gases "A" and "AB" is shown in Figs. 8 and 9, in terms of the compressibility factor, $PV/RT$, and pseudo reduced temperature and pressure. The pseudo reduced temperature or pressure is the ratio of the absolute temperature or pressure to the molal average absolute critical temperature or pressure of the mixture. The original data were cross-plotted to

Table V — Smoothed Volumetric Data

| Pseudo Reduced Temperature | | 0.70 | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 | 1.00 | 1.05 | 1.10 | 1.15 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compressibility Factor | Gas | Pseudo Reduced Pressure | | | | | | | | | |
| 0.9 | "A" | 0.065 | 0.100 | 0.120 | 0.140 | 0.155 | 0.185 | 0.225 | 0.260 | 0.320 | 0.410 |
| | "AB" | | | | | 0.150 | 0.230 | 0.335 | 0.385 | 0.410 | |
| 0.8 | "A" | 0.100 | 0.150 | 0.200 | 0.250 | 0.300 | 0.375 | 0.470 | 0.525 | 0.625 | 0.825 |
| | "AB" | | | | | 0.285 | 0.410 | 0.565 | 0.655 | 0.680 | |
| 0.7 | "A" | 0.120 | 0.185 | 0.260 | 0.335 | 0.425 | 0.545 | 0.680 | 0.775 | 0.930 | 1.170 |
| | "AB" | | | | | 0.385 | 0.555 | 0.730 | 0.850 | 0.900 | |
| 0.6 | "A" | 0.130 | 0.210 | 0.295 | 0.395 | 0.520 | 0.675 | 0.835 | 1.000 | 1.205 | 1.435 |
| | "AB" | | | | | 0.465 | 0.655 | 0.845 | 1.010 | 1.100 | |
| 0.5 | "A" | 0.135 | 0.225 | 0.320 | 0.440 | 0.590 | 0.775 | 0.970 | 1.200 | 1.425 | |
| | "AB" | | | | | 0.525 | 0.730 | 0.935 | 1.145 | 1.265 | |
| 0.4 | "A" | 0.140 | 0.225 | 0.335 | 0.470 | 0.640 | 0.850 | 1.085 | 1.350 | 1.600 | |
| | "AB" | | | | | 0.565 | 0.775 | 1.000 | 1.260 | | |
| 0.3 | "A" | 0.145 | 0.230 | 0.345 | 0.495 | 0.680 | 0.910 | 1.185 | 1.480 | | |
| | "AB" | | | | | 0.585 | 0.805 | 1.05 | | | |
| 0.2 | "A" | 0.150 | 0.235 | 0.350 | 0.510 | 0.700 | 0.950 | | | | |
| | "AB" | | | | | 0.600 | 0.825 | | | | |
| 0.1 | "A" | 0.155 | 0.235 | 0.360 | 0.525 | 0.715 | | | | | |
| | "AB" | | | | | 0.610 | | | | | |

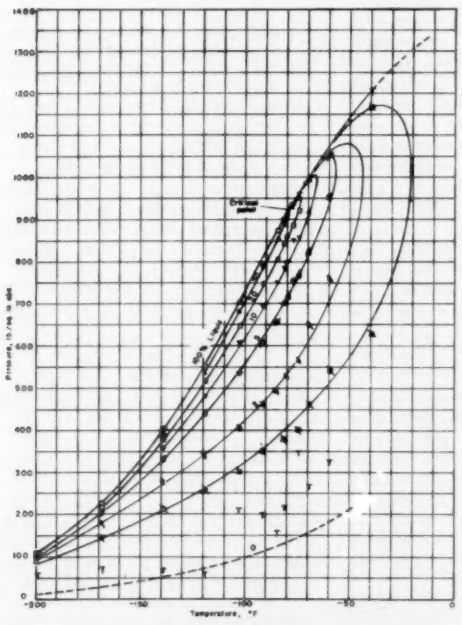


FIG. 6 — PRESSURE-TEMPERATURE PHASE DIAGRAM OF GAS "A"

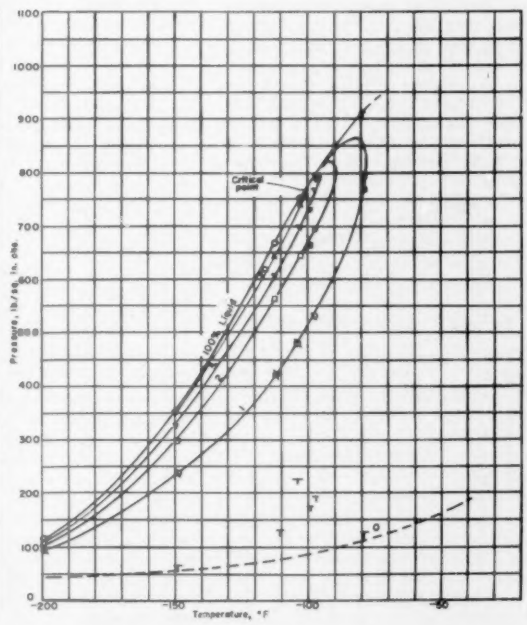


FIG. 7 — PRESSURE-TEMPERATURE PHASE DIAGRAM OF GAS "AB"

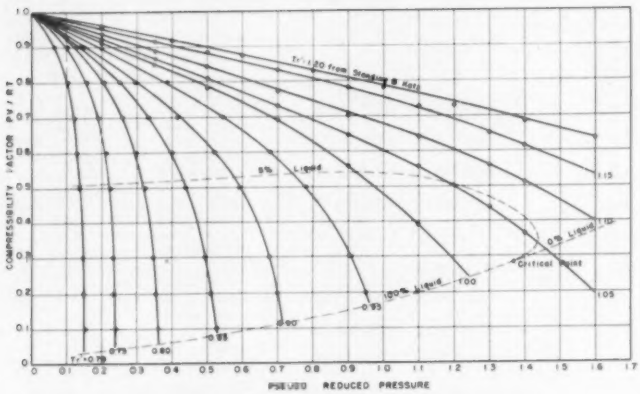


FIG. 8 — PRESSURE-VOLUME-TEMPERATURE BEHAVIOR OF MIXTURE "A"

even values of reduced temperature, and the points shown in Figs. 8 and 9 are read from the crossplotted curves. Values read from Figs. 8 and 9 are given in Table V.

The upper isotherms in Figs. 8 and 9 overlap the lower limit of the generalized correlation mentioned above, which extends to a pseudo reduced temperature of 1.05. Above a reduced temperature of 1.10 the agreement between these data and the generalized data is quite good at low reduced pressures, falling off at high reduced pressures. At the highest reduced temperature, 1.20 for gas "A" and 1.15 for gas "AB," these data and the generalized data are practically identical, as is shown by the fact that the upper line in each chart, while taken from the generalized data, fits the points from this study very well.

## ACKNOWLEDGMENT

The assistance of A. F. Bertuzzi, who aided in the computations and the experimental work, is gratefully acknowledged.

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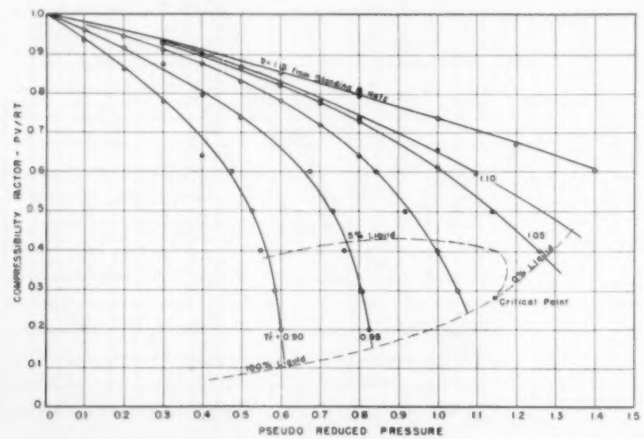



FIG. 9 — PRESSURE-VOLUME-TEMPERATURE BEHAVIOR OF MIXTURE "AB"

# The Drift of Things

. . . as followed by **EDWARD H. ROBIE**
**Secretary AIME**

### *Round Trip to Spokane*

September usually being a fine month for motoring, we set out with our better half at the end of August in our Studebaker for points west — a combined business trip and vacation. The first night found us 392 miles away, at the Statler Hotel in Buffalo, and the next morning we revisited Niagara Falls for the first time in some 40 years. The cataracts were as impressive as ever and certainly worth a day of any vacationist's time, instead of the half hour we could spare before going on to Chicago.

The Centennial of Engineering, the hundredth anniversary of the founding of the ASCE, no doubt no attracted the greatest gathering of engineers in history but still the attendance was disappointing to most of the 40 or 50 societies that participated. Perhaps the time — the two weeks following Labor Day — was unfavorable. Few could afford to spend ten days away from home and business at that time of the year. Fall meetings of the AIME normally attract far more than the 300 that registered in Chicago. The technical program, however, was excellent, especially that arranged by the Minerals Beneficiation and Industrial Minerals divisions. The mineral industry papers of a more general nature that were presented as a part of the Centennial program on Monday and Tuesday of the following week were of high quality and offered by top names but had a meager audience. Details of the program were unavailable at the time the August journals went to press, so advance publicity was inadequate, and most of the AIME crowd had departed over the week end.

Undoubtedly the celebration brought engineers and engineering to the attention of millions of people. The pageant at the Museum of Science and Industry proved continuously interesting, showing the progress of engineering following the first use of fire. The show continued for many weeks. A special stamp was issued by the Government, which engineers might well use on their Christmas cards or other mail this year.

After six days in Chicago we set out north, first visiting Fairbanks Morse in Beloit and Allis-Chalmers in Milwaukee. Will Mitchell's Basic Industries Research Laboratory is doing interesting work and being installed in more comfortable quarters. The next day at Ishpeming, C. W. Allen arranged for luncheon with a local group of AIME members and we then looked over the new surface plant of the Mather B mine, a model of modern functional design. Then on to a small dinner meeting at Calumet following cocktails at Endicott Lovell's attractive summer home on the lake at Point Mills. The new Memorial Union Building at Houghton, where we were domiciled for the night through the courtesy of Roy Drier, is a beautiful modern addition to the college, a model of its kind.

Lunch the next day in Duluth with a school days friend, Walter Maxson, who is heading Oliver Iron's taconite research, and then on to Virginia for an evening meeting of the Minnesota Section's Minerals Beneficiation group. An attendance of 85 testified to the success of the Minnesota Section's plan of bringing the AIME to local members on a Divisional basis. A Mining group is similarly active. Each holds about four meetings a year, these supplementing the annual meeting of the Section in mid-January in Duluth. The next morning was spent in revisiting some of the big iron pits on the Mesabi Range with Bill Taylor and C. J. Calvin, and then on to Grand Forks, N. Dak., for the night.

Grand Forks has a fine new Bureau of Mines building, to be devoted to fuel technology, and, of course, the University of North Dakota. A mining curriculum is well established, as is an AIME Student Chapter. Such well-known MBD'ers as Grover Holt and Joe Swainson graduated there. By nightfall the next day we were at Williston, where who should we run into but Charley and Eda Millikan, who the next morning, showed us over Amerada's well in the new and famous Williston basin, thereby considerably increasing our knowledge of petroleum production.

High spots of the next week started with a luncheon meeting with Columbia Section officers at Spokane. Incidentally, Spokane has a beautiful new modern hotel, the Ridpath, which we can recommend. Then on to Wallace for a dinner meeting with some of the Coeur d'Alene Subsection members. The next morning, a trip around the district and a visit to AS&R's new Galena mine. Lunch at the attractive new Florence Hotel at Missoula, and a never-to-be-forgotten dinner with Chester Steele and other Montana Section notables that night at Ted Treparisch's Rocky Mountain Cafe at Meaderville. No gambling left there but plenty of good food and drink. A little sightseeing the next morning on "the richest hill on earth" and in the afternoon into Yellowstone Park. A page or two could be devoted here to the pitfalls of visiting national parks after the season has closed.

The next day a trip of over 400 miles through Wyoming, winding up with a dinner meeting with a Wyoming Section group at Laramie, at the Diamond Horseshoe no less. And Saturday night down at Denver a fine meeting of the Colorado Section.

Then six days at the Mining Congress meeting, perhaps the biggest aggregation of mining men ever held, with a fine machinery show. It started Sunday afternoon with a trip to Golden to see all the new buildings and equipment at Colorado's world-famous mining school; and wound up, for us, on Friday with a trip to the famous mining district of a half century ago — Cripple Creek. This included a mountain trout luncheon at the Elks Club in Victor, underground in the Ajax mine, and a steak dinner at the famous Broadmoor in Colorado Springs.

Denver to Chicago took the better part of three days. Here the trip was punctuated by a flight down to Houston for the Petroleum Branch fall meeting. More than 1,500 men and close to 400 ladies attended, the Branch's biggest meeting ever. It is an earnest, young, live, and friendly group who have contributed a great deal to the progress of the Institute in the last few years. A fine buffet supper and water show at Glenn McCarthy's famous Shamrock.

And finally home. No accidents of any kind, nor did we even see one. Practically perfect weather, warm and only a couple hours of rain in five weeks. Some 6,700 miles covered, at 20.7 miles per gal actual mileage, 5 per cent less than the speedometer reading, most speedometers, including ours, being fast. Western highways are excellent and faster than in the East, but the Pennsylvania Turnpike, 325 miles long, the finest of all. A memorable trip. We are more than ever proud of our profession and our country. ★

# Personals

HAROLD VANCE, head of the petroleum engineering department of Texas A&M College, joined the staff of the Second National Bank of Houston, Tex., on Oct. 15, as head of the oil and gas division. Vance was born in Geneva, Ind., and has lived in Texas since 1926, having spent one and one-half years as a geologist with United Oil Co. in Los Angeles and one and one-half years with the U. S. Bureau of Mines in Casper, Wyo., after graduating from the University of California in 1923. He joined the Marland Oil Co. in 1926 as division petroleum engineer, and moved to Midland in 1929 as division superintendent of Continental Oil Co. Since 1931, he has been a consulting engineer and independent operator first in Kilgore, Tex., and, since 1934, at College Station in addition to his duties with Texas A&M.

+

HOLLIS D. HEDBERG has been named chief of the geology and geophysics section, land and exploration branch of the production department of Gulf Oil Corp. He will supervise and direct staff activities in the Pittsburgh office. Hedburg joined the company in 1928 as a stratigrapher and director of the geological laboratory in Maracaibo, Venezuela. He served as division geologist in Eastern Venezuela, and as assistant chief geologist in Mene Grande before his transfer to the New York office in 1946. Immediately prior to his recent transfer he was manager of exploration.

+

ROBERT L. BOGGS is now assistant to the vice-president, K. C. Heald, in the production department of Gulf Oil Corp. He has served with the company since 1927, when he was district engineer in the Tulsa production division. He worked as production engineer, chief petroleum engineer and executive assistant in Western Venezuela, and later was transferred to Caracas and San Tome with the Mene Grande Oil Co. He was elected vice-president and director of Mene Grande in 1949. Recently he has been manager of Western Hemisphere production operations in the Gulf Co.'s New York office.

+

JOE A. LAIRD, geologist and petroleum engineer, and for the past three years professor of petroleum engineering at Texas A&M College, has opened consulting offices at 1006 San Jacinto Building, Houston. For several years Laird served as geologist and petroleum engineer for George W. Strake, Houston independent oil operator and was also district engineer for the Texas Railroad Commission in Houston. He received his degree in petroleum engineering from Texas A&M and a master's degree in geology at the University of Oklahoma. He is a registered engineer and a member of the AAPG.

H. H. KAVELER has opened offices in Tulsa, Okla., for general consulting on oil and gas production problems. A graduate of the Missouri School of Mines and Metallurgy and of the University of Maryland, where he recived a PhD in chemistry, he later served on the faculty of both schools. He worked with the U. S. Bureau of Mines in Pittsburgh, and joined Phillips Petroleum Co. in 1936, serving in various capacities in the research, economics and production departments. He is the author of a number of technical and general papers, with particular emphasis on problems related to pressure maintenance operation and unit operations. Kaveler has also been active in the API and AIME, filling several committee assignments.

## *Charles F. Rand Medal Awarded to Holman*

William E. Wrather, chairman of the Charles F. Rand Foundation Award Committee, notified the Board of Directors at its Sept. 7 meeting that Eugene Holman had been nominated by the committee to receive this award at the Annual Banquet in 1953. The Board approved this nomination. The citation to accompany the award will be presented at the November meeting. ★ ★ ★

## *Sections Get Part Of Initiation Fees*

The benefit to Local Sections in obtaining new members is not only an increase in membership but also financial aid. It may not be generally known that a Local Section receives $2 of the initiation fee of each new Member, or Associate Member who resides in the territory of its Section. This does not apply to change of status nor to reinstatements. Until recently, only 10 per cent of any installment paid on the initiation fee was sent to a Section but now the full $2 is sent at once although the full initiation fee may be paid, if the member so wishes, in four equal installments. This addition to a Section's working capital should be an extra incentive toward obtaining new members. Checks are mailed to Local Sections at approximately quarterly intervals. ★ ★ ★

## *Southern California Students Elect Officers*

Dale E. Johnson, Los Angeles, has been elected president of the AIME Student Chapter at the University of Southern California for the current year. Other new officers are William D. Dockery, Compton, vice-president; Thomas M. McDonough, Los Angeles, recording secretary; Richard H. Butler, Inglewood, corresponding secretary; and Robert P. Boyle, Los Angeles, treasurer.

The students are holding monthly meetings with guest speakers from industry. Their plans for the year also include several field trips, and a Spring Meeting on the campus for students and men in industry. ★ ★ ★

## *1953 Robert H. Richards Award Announced*

At the Board meeting on Sept. 7, it was announced that Edward William Engelmann had been nominated to receive the Robert H. Richards award at the Annual Meeting in 1953. The Board approved the nomination and the accompanying citation which reads:

"For his outstanding accomplishments in advancing the technique of the metallurgy and beneficiation of copper ores." ★ ★ ★

# Proposed for Membership, Petroleum Branch

*Total AIME membership on Aug. 31, 1952, was 18,125; in addition 1,555 Student Associates were enrolled.*

ADMISSIONS COMMITTEE

*T. D. Jones, Chairman; Thomas G. Moore, Vice-Chairman; Harold S. Bell, F. W. Hanson, R. H. Chadwick, T. W. Nelson, J. H. Scaff, John T. Sherman, A. C. Brinker, Ivan Given, C. A. R. Lambly, G. P. Lutjen, E. A. Prentis, and C. Leslie Rice, Jr.*

*The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire as members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.*

*In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.*

## CALIFORNIA

**Burlingame** — Miller, James Merle (M).
**Long Beach** — Biren, Jack Ambros (M); Ritter, James William (J).
**Los Angeles** — Heintz, Louis O. (C/S-J-M); Peters, Ewald F. (M).
**San Fernando** — Evans, Charles Burton (J); Mesenbrink, Edward Damian (J).
**Santa Maria** — Trankle, Brian B. (J).
**Ventura** — Edgecomb, Clark Raymond, Jr. (M).

## COLORADO

**Denver** — Rowland, David A. (C/S-S-J).

## DISTRICT OF COLUMBIA

**Washington** — Heilborn, George (C/S-J-M).

## ILLINOIS

**Mt. Vernon** — Farrar, Fletcher F. (R,C/S-S-M).

## INDIANA

**Evansville** — Bradel, George P. (R,C/S-S-A).

## KANSAS

**Great Bend** — Olson, Dale C. (J).

## LOUISIANA

**New Orleans** — Pederson, Jan Nedland (M); Williams, James Albert (A).
**Shreveport** — Hollinger, George C. (R,C/S-J-M).

## MICHIGAN

**Grand Rapids** — Brady, John R. (J).

## MISSISSIPPI

**Jackson** — Welby, Charles William (C/S-S-J).

## NEW MEXICO

**Hobbs** — Wood, William D. (R,C/S-S-J).
**Santa Fe** — Lilystrand, Theodore O., Jr. (M).

## OKLAHOMA

**Bartlesville** — Bertch, Thomas M. (R,C/S-A-M); Berthelot, Byron Wayne (J); Kaufman, Milford James (R,C/S-S-J).
**Chickasha** — Cox, Byron V., Jr. (J).
**Oklahoma City** — Roberts, Eugene Curtis (J).
**Tulsa** — Horner, Victor Vernon (M); Kirschner, Robert Donald (J); Kliewer, Max Erwin (J); Koeller, Raymond Charles (J); McGaha, George Wayne (M); Mingee, James C. (J); Owens, William Wallace (J); Strand, James Allen (J); Strider, Haynes Leon (J); Sublett, James Dexter (J); Tracy, George W. (R,J).

## TEXAS

**Abilene** — Gray, Gordon H. (M); Lacik, Harold A. (M).
**Bay City** — Kimmel, Marion Leo (J).
**Bellaire** — Darling, Richard M. (R,C/S-A-M); Johnston, Guy H. (M); Phenicie, John W. (J).
**Big Spring** — Wilson, George N. (J).
**Breckenridge** — Bailey, Lee C., Jr. (M).
**Corpus Christi** — Allday, Fred White, Jr. (J); Bartgis, Guy Charles, Jr. (J); Carr, Cecil Harvey (J); Dickman, Wilfred Herbert (M); Emery, Maurice Neil (J); Johnson, Harlon Othell (A); Lewis, Donald DeWitt (M); McMahon, James J. (J); Smith, Sidney Horace, Jr. (M); Taylor, Austin Blackwood (J).
**Dallas** — Carlin, Russell Grant (M); Moore, James L. (R,J); Wilson, Robert (J); Wingate, Roy Gordon (C/S-S-J).
**Fort Worth** — Brown, Arthur K. (M).
**Houston** — Broun, Edwin Conway, Jr. (J); Brown, Thomas M., Jr. (M); Cashion, M. L. (M); Gibbs, Joe W. (M); Gilkeson, Paul Worth, Jr. (J); Gillespie, Darl D. (R,J); Grandall, Kenneth G. (R,C/S-J-M); Grest, Richard A. (M); Lawhon, Charles Floger (J); Phillips, Edward R. (J); Rowe, David Alan (J); Thompson, James Evan (J); Toelke, Lester William (M).
**Kilgore** — Banta, Thomas Alvin (J).
**Longview** — Browning, Carroll M. (J).
**Lubbock** — Hinchey, John Raymond (J).
**McAllen** — Britsch Clinton H. (J).
**McCamey** — Albrecht, Donald William (J); Rugg, Fred Edwin (J).
**Midland** — Daly, George D., Jr. (C/S-S-J); Goodrich, Alton C. (C/S-S-J); Merrion, James G. (J); Walker, William C. (A); White, Ven O. (C/S-S-J).
**Odessa** — Alexander, Herbert (J); Lynn, Bascom R. (C/S-S-J).
**Rosebud** — Jones, Ben L. (M).
**San Antonio** — Kotara, Lambert S. (J).
**Tyler** — Arnold, James Walter (J).

## VIRGINIA

**Annandale** — Graham, Gordon M. (C/S-A-M).

## WYOMING

**Midwest** — Mueller, Joseph Fred (C/S-S-J).
**Worland** — Strampe, Wesley E. (C/S-S-J).

## CANADA

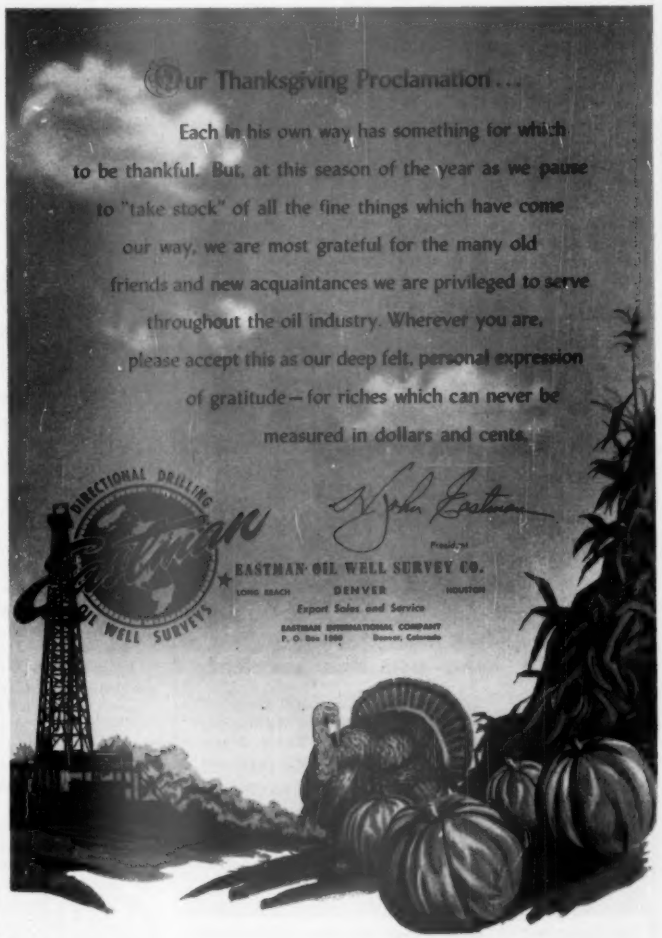
**Calgary, Alta.** — Humphries, Ralph G. (M); McDonald, James B. (C/S-S-J).

## SAUDI ARABIA

**Dhahran** — Drury, Harley Frederick (R,C/S-J).

## VENEZUELA

**Caracas** — Bake, Claude Leon (M). ★ ★ ★


Our Thanksgiving Proclamation...
Each in his own way has something for which to be thankful. But, at this season of the year as we pause to "take stock" of all the fine things which have come our way, we are most grateful for the many old friends and new acquaintances we are privileged to serve throughout the oil industry. Wherever you are, please accept this as our deep felt, personal expression of gratitude — for riches which can never be measured in dollars and cents.
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## *Petroleum Reservoir Mechanics*

*Continued from Page 27, Section 1*

creased by more than two-fold by increasing $a$ to 100 per cent. On the other hand, production may be increased markedly by increasing the number of rows of slots, $n$, from one to two or three.

These formulas and others like them do not tell us everything about reservoir mechanics. The assumptions necessary in their derivation, single-phase homogeneous fluids, uniform permeability, equal horizontal and vertical permeability, and no change in fluid properties as pressure on the fluid changes, are never found in field problems; so that these formulas are not useful for calculating the number of barrels of oil that a particular well will produce in a day. The formulas do, however, form a firm foundation upon which petroleum engineers can base their guesses. Almost all reservoir engineering problems can be considered as deviations from one of the formulas stated in the preceding paragraphs or from other similar formulas.

Potential theory literature contains a wealth of ideas, formulas and equations that might be useful to petroleum engineers. This literature is usually written, however, in language that is not readily understood by the practicing petroleum engineer; equations are expressed in mathematical terms that cannot be easily used by the engineer. Muskat has attempted to bridge the gap between this literature and the petroleum engineer, but his writings have not received the attention that would appear to be due them. Many of the problems and solutions to problems given in his books should be of immediate interest to practicing petroleum engineers, but many engineers still seem to be unaware of them. For example, few engineers are familiar with the Muskat Offset Formula which shows the bottom hole pressures that should be maintained in a pair of offset wells so that no oil flows across the property boundary between them.

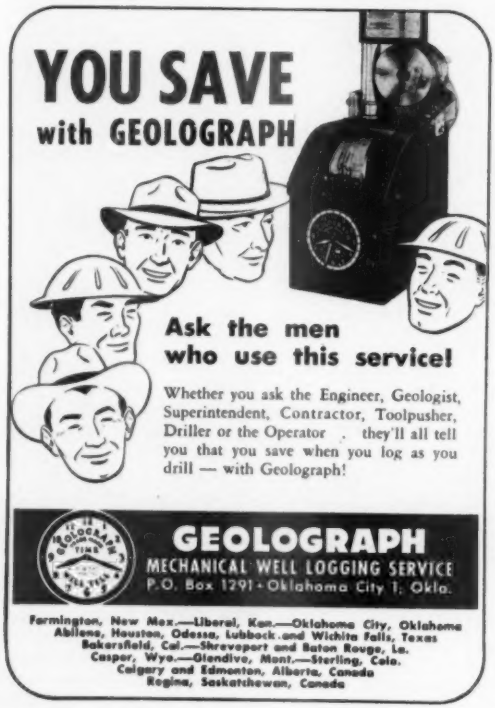
All of the theory that has been developed for the petroleum engineer has not been utilized by him; on the other hand, however, the petroleum engineer has presented the research worker with many reservoir engineering problems that he has not yet been able to solve. Almost all of the potential theory problems have been solved for the relatively simple condition of homogeneous fluid flowing in steady state. As soon as two or three fluids flow simultaneously, and as soon as the flow changes with time, problems cannot be solved by currently existing mathematical methods. Present-day production research is working hard to develop methods for predicting the transient flow that exists in oil wells and for using the two and three-phase flow measurements that are made on small cores to determine what happens in an oil reservoir. Because the mathematics of these problems are cumbersome and tedious, most of the work is being done with the aid of computing machines.

At the end of his talk, Cardwell entertained a discussion and question session. Almost all of the group of about 60 engineers present discussed particular parts of Cardwell's talk and asked questions concerning reservoir flow problems.

### REFERENCE

1. Muskat, M.: *The Flow of Homogeneous Fluids Through Porous Media*, McGraw-Hill Book Co., N. Y., 1st Edition (1937).

★ ★ ★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Casper, Wyo.—Glendive, Mont.—Sterling, Colo.
Calgary and Edmonton, Alberta, Canada
Regina, Saskatchewan, Canada

## *Clay Conference Abstracts*

*Continued from Page 24, Section 1*

overburden pressure, behave as cation selective membranes. A tentative electrochemical structure for shale is suggested.

The problem of the bi-ionic potential is considered and new equations presented to cover the varieties of bi-ionic potential which are likely to be involved in SP logging. The importance of cation exchange on the clays in shales is examined and it is noted that SP log data indicate either that the exchange constants of clays in marine shales are all similar or that they change only slowly with depth in a particular geological column. The problem of the shale baseline shift is examined.

If the calcium ion behaves towards shale membranes as a divalent ion, the formula previously proposed by the writer to compute interstitial water salinity from the electrochemical SP is likely to give a salinity which approximates the monovalent ion salt content of the interstitial water. Thus the formula should preferably be applied only to waters which possess a high primary salinity.

The problem of the electrochemistry of sands containing interstitial clays is considered from the standpoint of the Meyer-Sievers-Teorell equation. For optimum log interpretation in shaly sands, it is stressed that saline muds should be used.

The effect of shale content on the resistivity of permeable rocks is considered. Equations that have been proposed for such shale effects are discussed. It is pointed out that the effects of cation exchange and clay dispersion have been ignored and that the entire problem of shaly sands and their resistivities merits further study. ★ ★ ★

## Los Angeles Meeting Attendance Highest Yet, 593 Register for Technical Program

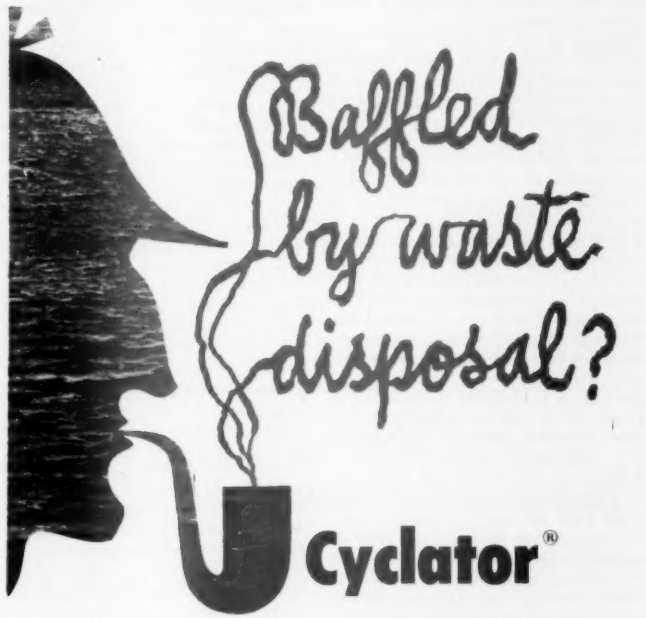
The Petroleum Branch meeting in Los Angeles on October 23-24 attracted the largest attendance of any of the petroleum regional meetings that have been held there. A total of 593 persons registered, where the attendance last year was 312. A large percentage of these consisted of non members. The two apparent reasons for the large increase were that the meeting was held in the downtown area in the new Statler Hotel, and the continuing expansion of the industry and profession on the West Coast.

A well-balanced program of eleven papers and one panel discussion was the highlight of the meeting, and also one of the factors causing the increase in attendance. Milton E. Loy, vice-chairman of the Branch Technology Committee for California, and program chairman for the Los Angeles meeting, had devoted a great deal of effort to arranging the program. He conducted a survey earlier in the year to determine the wishes of members regarding the program, and then arranged the program accordingly. The result was a well balanced program between research and operations, and between various fields of the technology. A number of members expressed appreciation for it.

Two luncheon addresses were well received. The first, by Frank P. Doherty, a Los Angeles attorney and civic leader, was an inspirational address entitled "Yesterday, Today, and Tomorrow," presented at the Pacific Petroleum Chapter luncheon. Its theme was that both labor and management (or business) have made significant contributions to the development and welfare of this country, and will continue to do so, but that their maximum future contribution will come only through strict observance of the principles of right and wrong on both sides. The second address, presented at the Southern California Local Section luncheon on Friday, was by J. R. "Bill" Pemberton, a West Coast petroleum consultant. It dealt with the future demand and supply for oil on the Coast, and expressed Pemberton's prediction that there will not be a shortage of oil in the West for a number of years to come if the industry is given the proper freedom of operation and control. ★ ★ ★

### *New Rule for Transfer To Junior Membership*

T. B. Counselman, chairman of the Membership Committee, has requested the Board of Directors to reconsider its action of Feb. 17, 1952, requiring that the signature of the original member sponsor be reobtained on the application for Junior Membership plus one more member's signature. The Board discussed this matter at great length and finally voted that hereafter a Student Associate applying for Junior Membership shall obtain only one member's signature, such signature to be other than that on his application for Student Associate. However, if he does not transfer in the year of his graduation, he must obtain the usual three members' signatures. ★ ★ ★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# Employment Notices

The JOURNAL will post notices of men and jobs available. Companies and AIME members are invited to use this space, for which there is no charge. Except as noted below, address replies to: Code (appropriate number), JOURNAL OF PETROLEUM TECHNOLOGY, 408 Trinity Universal Bldg., Dallas 1. Show return address on envelope. These replies will be forwarded unopened and no fees are involved.

Replies to the positions coded P-1, P-2, P-3, Y-7705, Y-7651, and Y-7626 below should be addressed to: Engineering Societies Personnel Service, 8 West 40th St., New York 18, N. Y. The ESPS, on whose behalf these notices are published here, collects a fee from applicants actually placed.

PERSONNEL

♦ Petroleum geologist, graduate, eastern college. Age 35, married, two children. Experience subsurface in Southwestern U. S. and Western Canada. Seven years' surface and subsurface Appalachian Geosyncline, including water-flooding, reserve estimates, evaluations. Member AAPG and API. Desire change of situation in exploitation or subsurface exploration Rocky Mountains, Eastern or Western Canada. Code 174.

♦ Engineer, 33, married, one child, desires change of position. Graduate with seven years' oil field experience in production, drilling, workover and general petroleum engineering. Preference is for supervisory position in production and/or drilling operations, or will accept position in engineering if proffered. Code 175.

♦ Geologist, age 36, master's degree, desires to relocate with small active independent preferably in Rocky Mountains or Texas. Seven years' diversified experience in all phases petroleum geology and well engineering in Southwest Texas, Mississippi, Louisiana and Alabama. Presently employed by large independent. Code 177.

♦ Petroleum engineer, University of Oklahoma, age 31, four years' experience drilling, well completions, gas compression and transmission, equipment sizing and purchasing. Interested in small active independent in Texas or Rocky Mountain region. Presently employed with drilling and producing company. Code 176.

♦ Geologist, AB, MS, eastern university. Experienced seismic interpreter with knowledge of subsurface geologic methods. Desires position as geologist. P-1.

♦ Production engineer immediately available for employment. Five years' production engineering experience including well completion, evaluation and reservoir studies with both major and independent oil companies. Age 32, married. P-2.

♦ Geologist, 27, married. Experience covers mining geology, experience in surveying, prospecting, mapping, geological drawing, recording pump performances, calculating feed belts, sampling, running float tests, recording prospecting data on 40-sheets; various mining calculations and making out production reports. Available three weeks' notice. P-3.

POSITIONS

♦ Registered professional engineers experienced in evaluation of oil and gas properties needed by major oil company headquarters in Tulsa. State experience and qualifications. Write direct to P.O. Box 521, Tulsa, Okla.

♦ Field and service engineer, under 30, graduate mechanical, who is interested in going in to the lubrication field. Training period in New York. Should have some previous sales experience. Considerable traveling. Possibility of relocating in Detroit in year or two. Headquarters, New York, N. Y. Y-7705.

♦ Piping designers and instrument specifications engineers experienced in the design of petroleum refinery facilities. Location, Ohio, Oklahoma and New Jersey. Y-7651.

♦ Construction superintendent, not over 45, ME or CE degree, with at least ten years' experience in heavy construction involving a considerable length of time in full charge of the projects. Must have had petroleum refinery or heavy industrial chemical plant experience. Will be 100 per cent field work at the actual construction site. Salary, $7,200-$7,500 a year plus expenses. Locations, throughout the United States. Y-7626. ★ ★ ★

## *U. of Houston Students Serve at Fall Meeting*

The membership of the newly formed student chapter at the University of Houston demonstrated their interest in AIME activities at the Petroleum Branch Fall Meeting in Houston on October 1, 2, and 3, 1952. This chapter is less than one year old, having been formed in February, 1952. Thirteen members turned out to assist the Arrangements Committee at the Petroleum Branch Meeting. Since being formed, this chapter has been well represented at the Gulf Coast Section general meetings and study groups. The faculty sponsor is C. V. Kirkpatrick, chairman of the petroleum engineering department. ★ ★ ★

## *Institute Installs New Addressing Equipment*

Modernization of operations at AIME headquarters called for new addressograph equipment. The change-over to the new stencils was completed in time to run the wrappers for the October issues of the Institute journals. In changing the tabbing on 20 thousand stencils, it is possible that some mistakes were made. If you did not receive your journal this month, or if you received the wrong journal, or too many copies, please write direct to AIME, 29 West 39th St., New York 18, N. Y. ★ ★ ★

## *Recommendations for Kelvin Medal Wanted*

Secretary E. H. Robie has received a letter from the Secretary of The Institution of Civil Engineers in London, England, requesting from each of the leading engineering societies in all parts of the world a recommendation for the award of the Kelvin Medal in 1953. This medal, which was awarded for the first time in 1920, is presented triennially as a mark of distinction in engineering work or investigation of the kinds with which Lord Kelvin was especially identified. Although Lord Kelvin was pre-eminently a pioneer in the study of pure physics, he also achieved a great deal in the application of pure science to the solution of engineering problems. It is stressed, therefore, that the medal is awarded to men of distinguished service in the application of science to engineering rather than in the development of physical science itself. The AIME has been requested to send before Feb. 1, 1953, a recommendation for this award. A short statement of the grounds upon which the recommendation is made should accompany the nominations. Secretary Robie will be glad to consider any recommendations from AIME members for presenting to the Board for a final selection. ★

## *Oil Development in Chile*

*Continued from Page 18, Section 1*

barytes, for additional weight. In the lower part of the hole the mud is generally kept to 10 lb per gal, 50-60 seconds viscosity and six cu cm or less water loss (30 min).

Rock bits are used throughout the hole. Between 50 and 90 days are required per hole depending on the equipment used, well completion, and transportation time.

Of the nine existing fields, five are gas-condensate fields with a thin black oil belt, two are oil fields with gas caps, one so far as is known is a gas-condensate field and in one no gas cap has been found so far, although it is suspected that one exists.

The Springhill sand which is the only producing sand in this area is a white, "sugar sand," medium to fine grained, cemented at times with silica or clay. Permeability varies from 0 to 1,000 md and thickness from 0 to 120 ft.

There is evidence of a partial water drive in all the fields. Bottom hole temperature is fairly constant at 240°F and bottom hole pressure is close to 3,250 psi in all fields. The oil ranges from 40° to 50° API, and is a mixed base crude with a high paraffin content.

With the exception of Manantiales, volumetric withdrawals from the producing fields have been such as to maintain the original bottom hole pressure at close to its original value.

A gasoline plant has recently been completed at Manantiales which includes a repressuring plant, a crude oil stabilizer and a small topping plant.

It is connected to the other fields by a six-inch and eight-inch gas line and a six-inch oil line. The plant capacity is 30,000 Mcf/D.

It is planned to repressure the Manantiales Field and maintain pressure in the other fields by means of this and other auxiliary plants.

Although oil was discovered in 1945, production was delayed until the latter part of 1949. In this interval an eight-in. pipe line was laid from Manantiales to Caleta Clarencia at Gente Grande Bay. A Marine Terminal was built there, and 27 additional wells were completed in the Manantiales Field.

Present daily production is 2,500 bbl from six fields. With the installation of the repressuring equipment it is anticipated that production will be increased. Production up to and including the first half of 1952 is as follows, in barrels:

| 1949 | 1950 | 1951 | 1st ½ 1952 |
|---|---|---|---|
| 55,300 | 629,775 | 758,500 | 404,077 |

Since the inception of production the oil has been sold to the "Administración Nacional de Combustibles, Alcohol y Portland" of Uruguay.

Exploration activities of the company include two geophysical parties, one of which is company owned and operated. The other is under contract with United Geophysical Co., who in addition to the equipment, furnishes a party chief and two assistants. A gravity meter party and a magnetometer party are also maintained. Ramón Laval is in charge of the geophysical work for the company.

The geological work directed by John S. Barwick includes a micropaleontological laboratory and a subsurface study group. As a rule there are four geological field parties operating during the summer months. Both the geological and geophysical work has been hampered by the inclement weather and the lack of roads. The mantle of glacial material covering a good part of the area has made seismograph interpretation difficult and has confined outcrops to the stream beds and coast lines.

In spite of this, the record of strikes has been very good. Out of 14 wildcats drilled since 1945, nine have resulted in oil or gas fields.

### ACKNOWLEDGMENT

The writer wishes to express his appreciation to the Empresa Nacional del Petróleo for permission to publish this article.

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# Book Reviews

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### Electronic Analog Computers

*By Granino A. Korn and Theresa M. Korn. McGraw-Hill Book Co., New York, first edition, 1952. 378 pp., illus., diag., 9¼ x 6¼ in., bound. $7.00.*

Following an introductory chapter, the book describes practical setup procedures and the application of d-c analog computers to representative practical problems. The theory, design, and operation of linear computing elements, amplifier circuits, and control circuits are covered in a practical maner. Developments in the field of analog multiplication and function generation are discussed, and the design and construction of complete computer installations are given for various applications in industry and science. The book constitutes a manual which is intended to promote the effective operation of d-c analog computers by anyone whose mathematical background covers elementary differential equations.

### Principles of Geochemistry

*By Brian Mason. John Wiley & Sons, Inc., New York, 1952. 276 pp., charts, tables, 9¼ x 6 in., bound. $5.00.*

Following a description of the subject matter and scope of the book, the author presents a logical account of the earth's pre-geological history, utilizing new data on the abundance of elements and isotopes in the earth and the universe. Such questions as the geochemistry of igneous, sedimentary, and metamorphic rocks, the origin and evolution of the ocean, and the role of organisms in the concentration and deposition of individual elements are discussed in detail. The book stresses the need for greater effort in interpreting the data of geology in terms of the principles of physics and chemistry.

### Combustion, Flames and Explosions of Gases

*By Bernard Lewis and Guenther von Elbe. Academic Press, Inc., New York, 1951. 795 pp., illus., charts, tables, 9½ x 6½ in., cloth. $13.50.*

Part I of this extensive treatise deals with the chemistry and kinetics of the reactions between oxygen and the following fuel gases: hydrogen, carbon monoxide and various hydrocarbons. Part II, comprising about one-half of the text, provides an exhaustive treatment of flame propagation, covering combustion and detonation waves, ignition, fuel-jet combustion and flame photography. Part III examines the state of the burned gas and Part IV discusses the relation of the foregoing to a variety of technical combustion processes such as industrial heating and internal-combustion engines.

### Business and Professional Speech

*By L. Crocker. Ronald Press Co., New York, 1951. 463 pp., charts, tables, 8¼ x 5½ in., cloth, $4.00.*

A detailed treatment of the basic aspects of speaking before an audience or group, covering grammar, selection of material, presentation of ideas, etc. Part II presents examples of common types of business and professional speeches. Appended are a bibliography and a section on suggestions to teachers.

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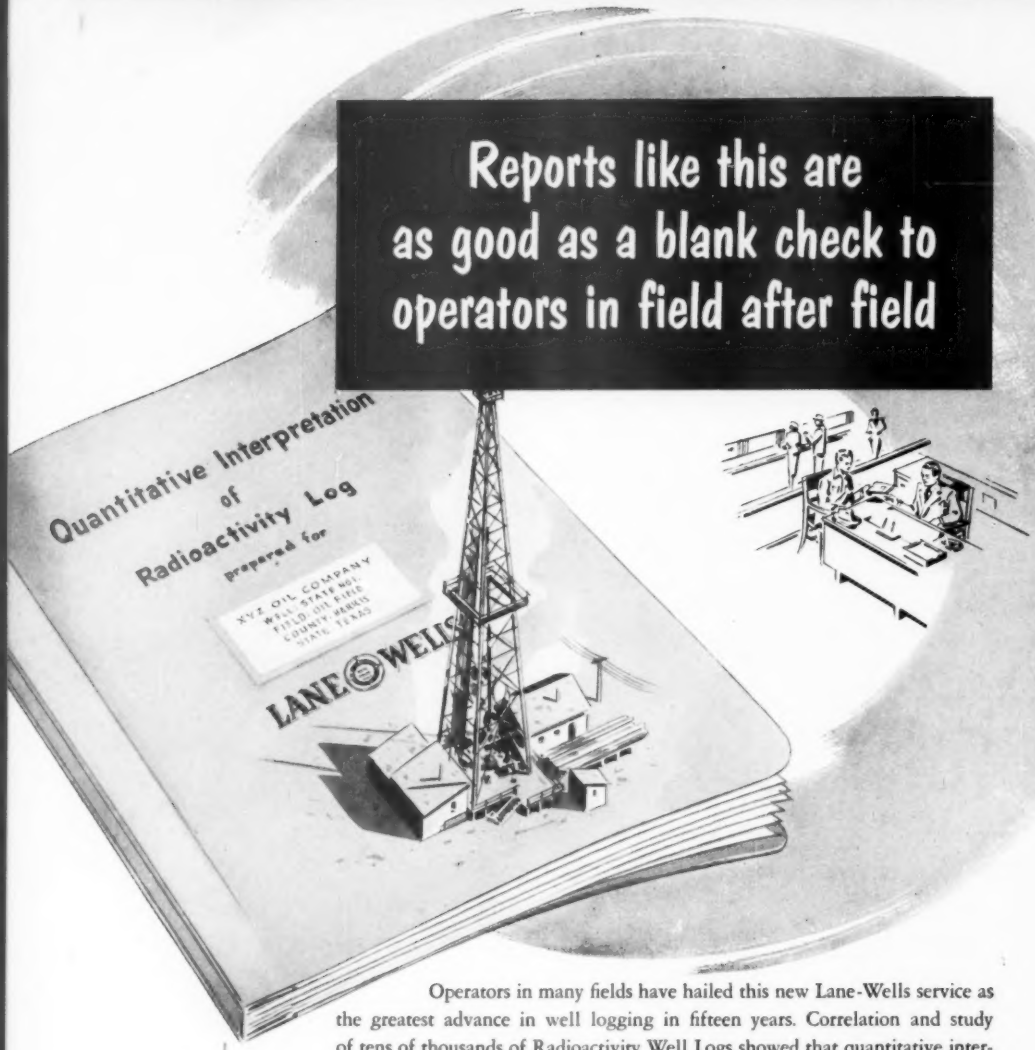


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